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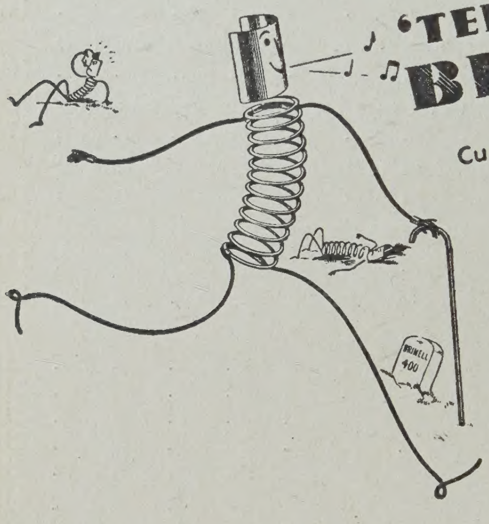

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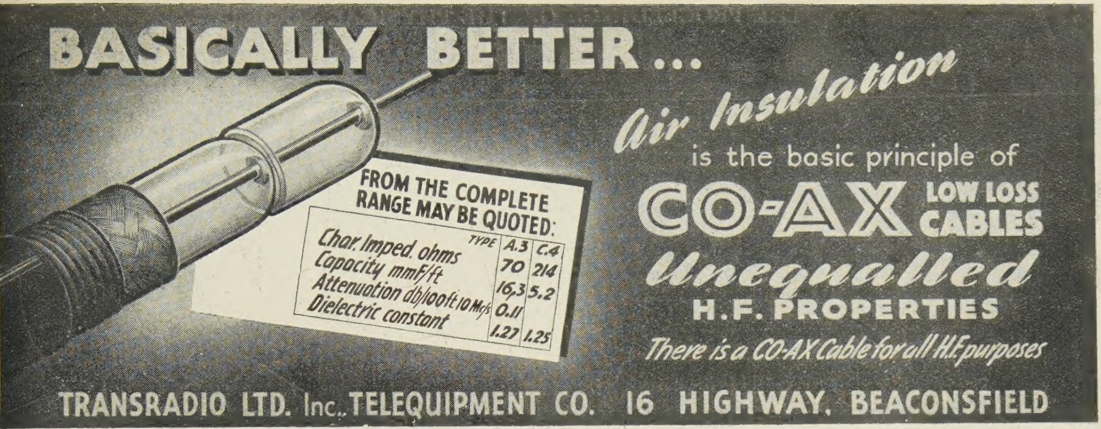

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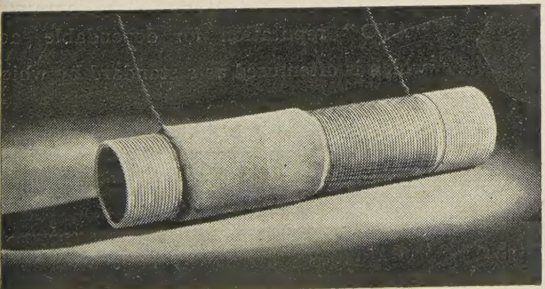

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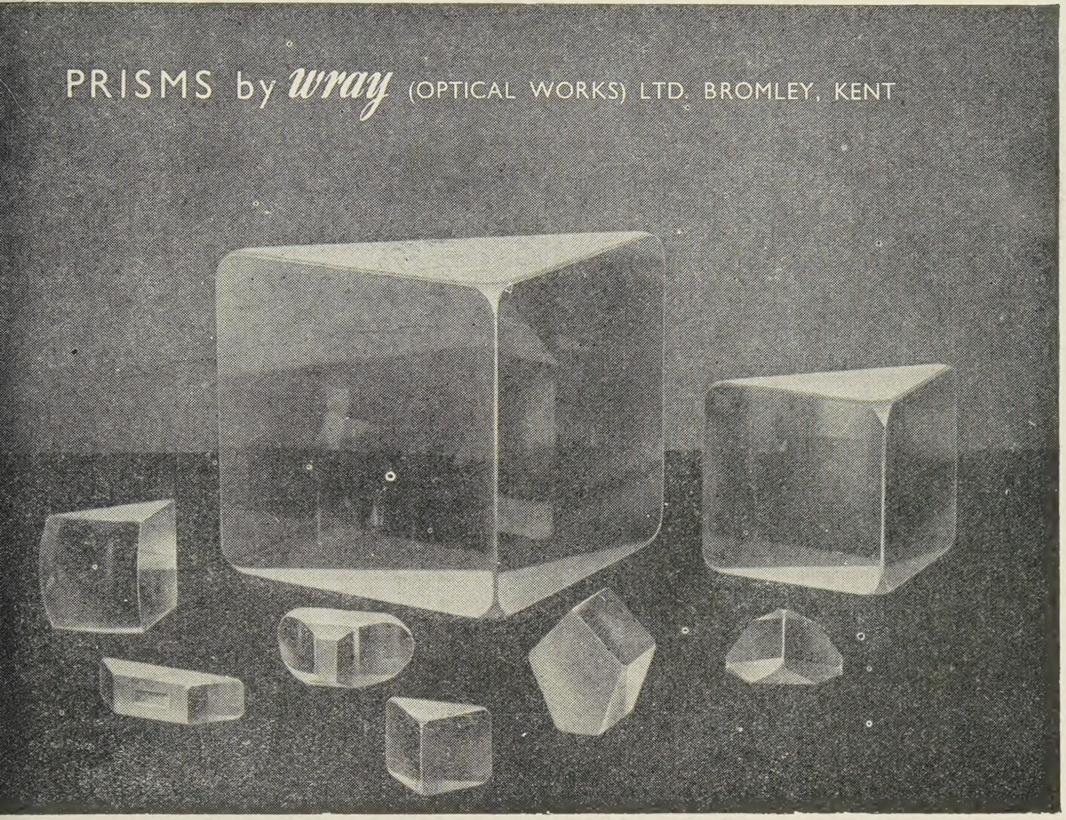

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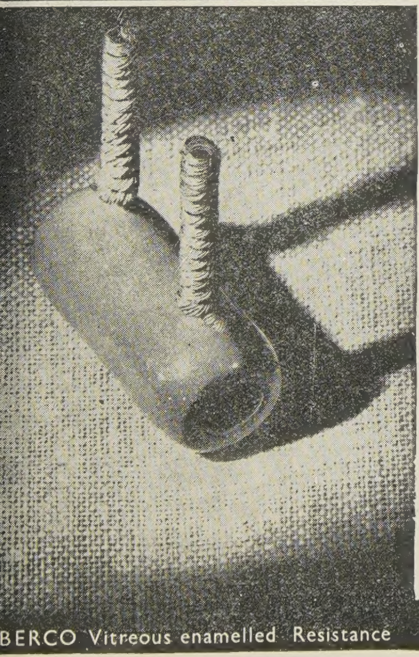

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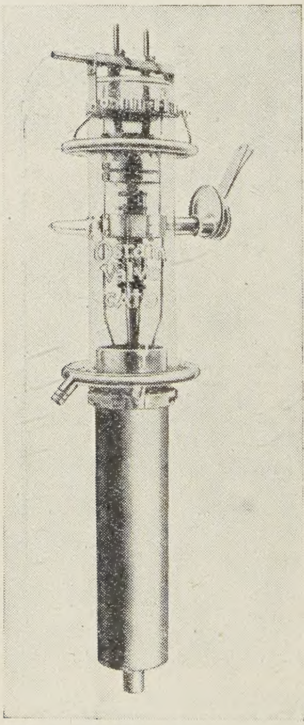

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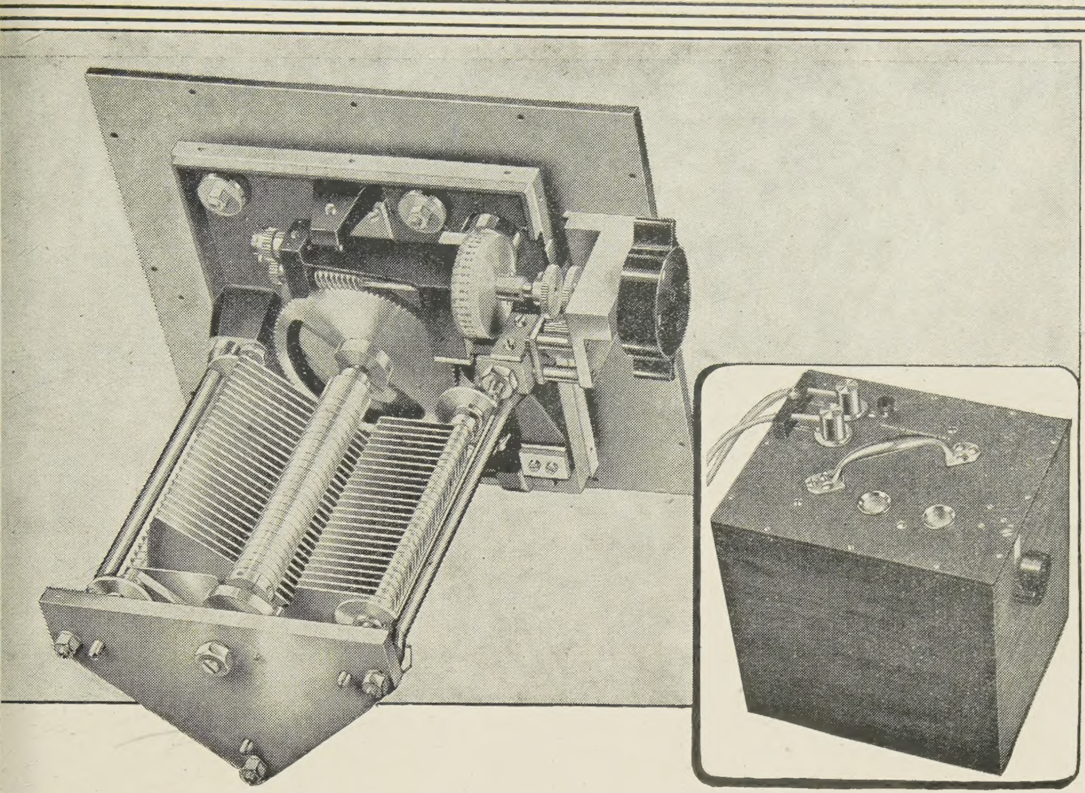

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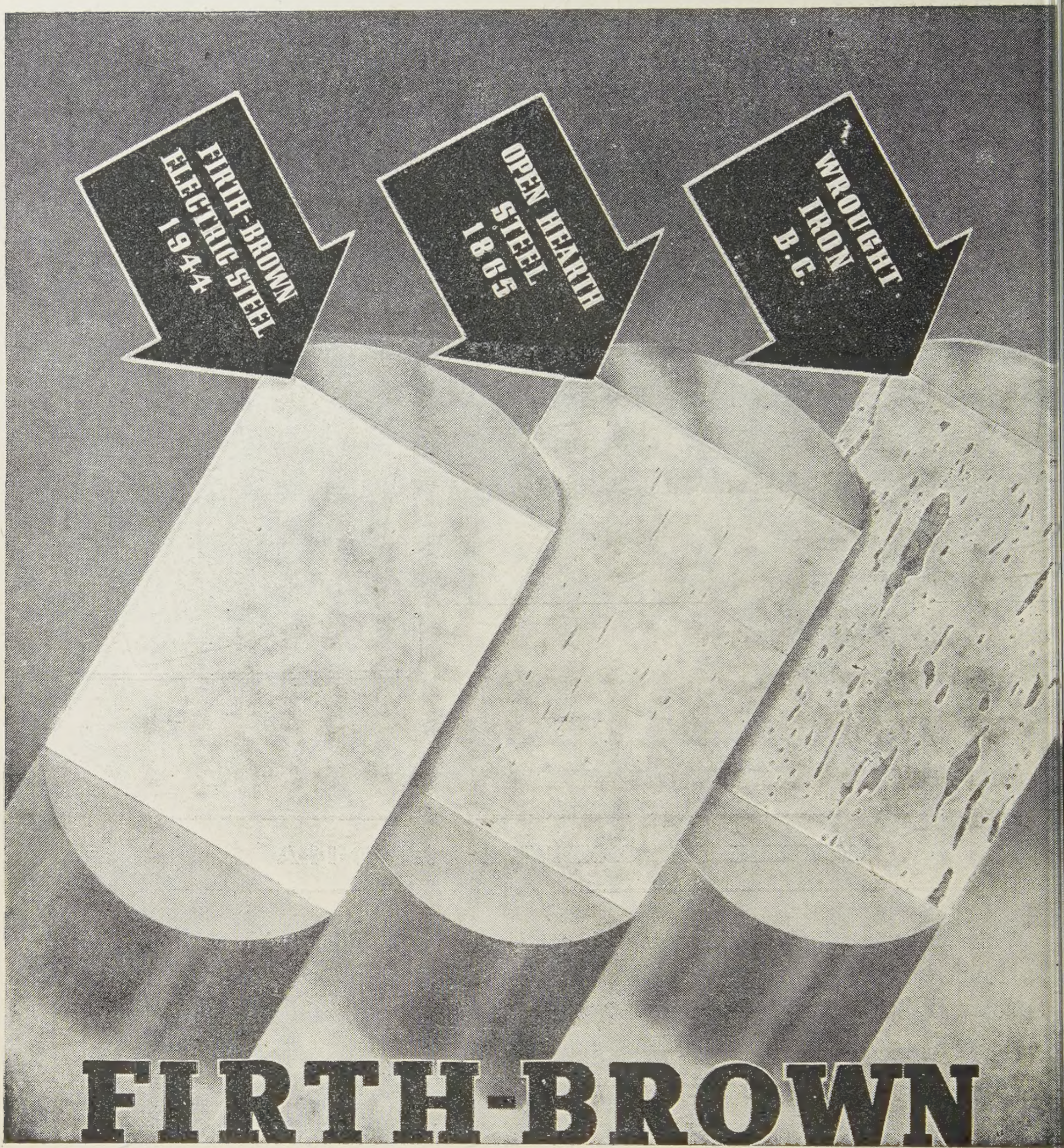

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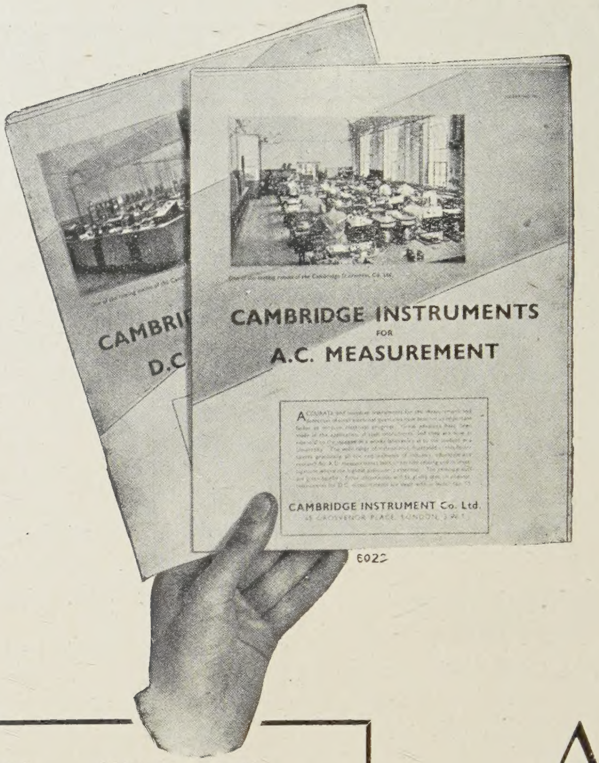

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A SURVEY OF NUCLEAR FIELD THEORIES

BY H. T. FLINT,
King's College, London

Lecture delivered 26 *November* 1943

§ 1. INTRODUCTION

BEFORE embarking upon the consideration of the nuclear field theory let us recall briefly the general character of field theories.

The best known theory of this kind is that of Maxwell—the theory of electromagnetism. It may be described as a complete field theory, for it is based upon certain quantities, the electric and magnetic intensities, by means of which the properties of the field are described. These quantities satisfy certain field equations. The energy and electro-magnetic momentum are expressed by means of the quantities, and these satisfy other relations which express the principles of conservation of energy and momentum.

Maxwell's theory goes into the question of the origin of the field, and it is possible to determine the field intensities from electric charges and their motion. These are the generators of the field. A formal simplification results from the introduction of the scalar and vector potentials, from which the field intensities can be deduced; and the simplest approach to the study of the field is to express these potentials in terms of the charges.

There is another type of description which is an abbreviated form of field theory. In this case, the field intensities do not appear, and the expressions for the energy and momentum are obtained without the use of intensities. This hardly merits the title of field theory, but the energy is expressed as an energy density and the total value is obtained by integration over a region. Hydrodynamics exemplifies this type of theory, as does the relativity theory of continuous matter.

In the quantum theory the latter hydrodynamical type is used in the field theory of the electron, and the former is the basis of the theory of the meson.

A field theory of the Maxwell type was introduced early in the development of the new quantum theory. It was originally proposed as a theory of the electron, and it seemed at first that it might offer another aspect of the quantum theory of that particle. An important feature was that it introduced the idea of a magnetic moment which was to be associated with the particle, and it suggested a value known to be correct. But it appeared later on that the mechanical moment of momentum or spin which the theory proposed was incorrect. This feature was regarded as showing the essential inapplicability to the electron. At that time, just before 1930, only two ultimate particles had been discovered, so that there was no apparent use for this particular form of field theory. For a time the study of it was almost given up. Some years after the first attempt, the theory was discovered again by Proca, who, however, now called it a theory of positrons and electrons. He brought out a new feature of the theory, but it was still not a theory of these particles. Shortly after this, Yukawa, a Japanese physicist, used the same field theory as a description of the field generated by the nucleus. He appears to have derived the field equations solely on the analogy with Maxwell's equations without knowledge of the earlier work in this direction. The important feature in this case is that his applications of the theory show that the particle which previous writers had associated with the field was incorrectly described as an electron. The mass of the particle was 100 to 200 times that of the electron. Yukawa speaks of it as a " light quantum " in contrast to the heavy quanta, by which he means protons and electrons. We now speak of it as a *meson*.

A striking sequel to this work was the discovery, in photographs of cosmic-ray tracks about two years after Yukawa's first paper, of a particle with range and momentum corresponding approximately to this mass. The particle, according to the theory, has to be associated with zero or integral spin, i.e., $n\boldsymbol{h}/2\pi$, not $(n+\frac{1}{2})\boldsymbol{h}/2\pi$, and that is what experiment requires.

It is proposed in this survey to give an account of the work which led to Yukawa's conclusion, for his important result, as is almost always the case in physical research, rests upon repeated attempts and upon the successes and failures of many contributors.

§ 2. THE WORK OF FERMI

Fermi's theory of β-ray disintegration is the pioneer work in this field of research. This theory is a field theory, although its essential character is not at once clear because attention is directed to the solution of a particular problem. Later workers have made use of the ideas introduced by Fermi; all of them have been influenced by his work. Let us examine the problem Fermi tried to solve. The characteristic of β-ray disintegration is that when the number of particles emitted from a radioactive substance is plotted against the energy they possess, a continuous curve is obtained. The curve extends from small energy values to a definite upper limit characteristic of each element. From the data collected by Sargent it appears that in each case the curve comes down to a definite end-point characteristic of the emitting element. The maximum of the curve is about one-third of the way along this axis of E, i.e. at $\frac{1}{3}E_m$.

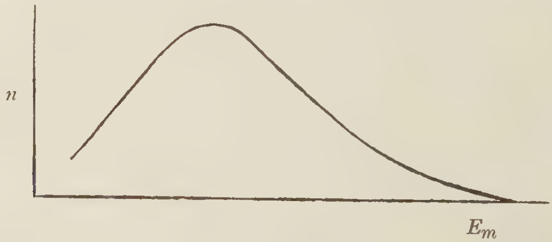


Figure 1.

The continuous energy distribution might be regarded as the result of the absorption of energy as the particles escape from the parent element. In that case it would be imagined that the particles all start with the energy E_m. Some manage to get through without loss, and they indicate the total original energy, which would be nE_m, where n denotes the number of particles emitted. There is a favoured energy of escape corresponding to the maximum of the curve. On the alternative view, that the particles are emitted from the parent element with the varying energies of the curve, the total energy they possess is $n\overline{E}$, where $\overline{E}$ is the average energy taken from the curve.

Experiment decides between the two possible values for the total energy. The work of Ellis and of others after him has shown conclusively by calorimetric measurements that the energy is equal to the average value $n\overline{E}$.

This appears to mean that the β particles leave the parent nuclei with different energies. Thus the apparently similar nuclei which result from the disintegration have different energies. This means that the possession of different amounts of energy in identical nuclei is of no significance, and amounts to a breakdown of the principle of conservation of energy in these nuclear processes. This might be the explanation of the difficulty, and it was an explanation offered originally by Bohr. It would mean that the energy principle which is recognized as valid on a large scale is an average result, but is not to be applied to this process in small-scale phenomena, although it appears to hold for all other individual atomic processes known to us.

Some other explanation is naturally sought, especially as there is another equally impressive difficulty. This concerns the principle of conservation of angular momentum. In order to explain a number of facts in spectroscopy, it has been found necessary to associate the particles, proton, neutron, positron and electron, with a certain angular momentum. In each of these cases the magnitude is $(\frac{1}{2}) \cdot \boldsymbol{h}/2\pi$, and all applications of this assumption lead us to suppose that the principle of conservation of angular momentum holds. Suppose that the number of particles in the nucleus is odd, it remains odd after the emission of a β particle. Thus, if there is any change in angular momentum in the nucleus, the magnitude is a whole multiple of $\boldsymbol{h}/2\pi$. The electron, however, carries away $\frac{1}{2} \cdot \boldsymbol{h}/2\pi$. The same difficulty arises if the number of particles in the nucleus is even.

There are thus two difficulties of a deep-seated character confronting the view that β disintegration consists in the simple emission of a β particle from the nucleus.

It appears that on account of the difficulty of spin, more than for any other reason, Pauli suggested that the process is associated with the emission of energy and momentum in a form which has so far escaped notice. He suggested that a neutral particle called a *neutrino* was associated with the emission. This particle has spin $\frac{1}{2} \cdot \boldsymbol{h}/2\pi$. The parent nucleus provides a certain amount of energy equal to the maximum of the β-ray spectrum, and this is divided in some way betwen the two particles.

The principles of conservation are maintained and the problem becomes that of determining how the energy is divided between the electron and neutrino.

§ 3. STRUCTURE OF THE NUCLEUS

In the attempt to form a field theory applicable to the nucleus it is essential to have a clear idea of its composition.

The old concept was that of a nucleus containing protons and electrons, but the later stages of the development of the quantum theory have shown that this is not merely insufficient, but is untenable. Some of the reasons are:

(1) Particles of the mass of the electron would have within the nucleus kinetic energies much greater than the binding energies of the nuclei. It is not at all probable that such a state of affairs could exist.

(2) The magnetic moments of electrons are for each $he/4\pi mc$, while the moments of the whole nucleus are much smaller than this.

(3) In the case of some nuclei (e.g. Cu) both electrons and positrons are emitted. Thus we should have to assume that they are both present in the small space of the nucleus. Under these conditions there is a high probability of their union to form a gamma ray, and it does not appear that they could occupy the nucleus together.

The point is essentially that if these particles were assumed to exist in the nucleus, that assumption would be inconsistent with the principles on which the quantum theory is founded. The position would be comparable with that which existed in the late stages of the theory of the aether. Conclusions would have been reached in contradiction to the main doctrine.

For this reason it is assumed that the atomic nucleus consists of protons and neutrons. These have almost equal masses, and they are not regarded as actually different particles, but as representing different states of the same thing. One state may pass into another: a proton may become a neutron and *vice versa.* We can say that there is a force of interaction causing them to change their rôles, and we can describe it as an exchange force. If a neutron becomes a proton, a negative charge must appear somewhere. The conclusion is that in the interaction a charged particle is generated. The first idea was that an electron and a neutrino appeared when a neutron became a proton, and a positron and a neutrino in the reverse transition. Thus the interaction of the heavy particles is represented by the appearance of the light particles, and the theory of β-disintegration should give information about the nature of the exchange force.

This concept of the nucleus and of β-ray activity is the basis of Fermi's theory. It provides us with a model for the process just as the nucleus and extra-nuclear electrons provide us with the Rutherford model from which to study the emission of light and X rays from the atom.

Fermi uses the theory of emission of these rays as an analogy for the present problem.

The generation of photons arises from the transition of an electron from one state to another in the atomic orbits.

We do not think of the photons as present all the time in the atom awaiting release. They are generated as a result of, as an accompaniment to, electron transitions. If a photon emerges as a result of an atomic impact we do not think of the photon as simply knocked out of the atom. In fact a certain time elapses between the impact and its appearance. This is also true when a β particle is generated as a result of nuclear impact, The analogy is that in β radioactivity the β particles correspond to photons and the nucleus to the atomic system of electrons. In the quantum theory of photon emission, the initial state is one in which there are electrons and no photons, and the final state is one in which the electrons have changed their states and photons are present. The object of the theory is to derive the probability of the transition from the first state to the final state. In the result the co-ordinates which appear are those of the electrons. We do not seek to localize the photons. In carrying out the analogy, Fermi introduces the co-ordinates of the nucleus but not that of the β particles and neutrinos.

In the case of the photons, the forces between the electrons and their interaction with the field of the photons are known, for the process follows laws with which we are familiar.

Very little is known about the forces in the analogous case, i.e. we do not know the interaction between the heavy particles and their interaction with the emitted particles. It is necessary to begin by making simple hypotheses to aid the representation and to arrive at the order of magnitude of the interactions. Some experimental evidence is available, of which we can make use.

There is one advantage in this type of theory. The kind of representation within the framework of the quantum theory is comparatively restricted, especially if we require simplicity. The notation may not be generally familiar, but the physical concepts are simple.

In the first attempt the forces were supposed to depend *only upon the co-ordinates* of the heavy particles. They might depend upon their velocities, accelerations and spins, but these are omitted. The analogy with the generation of photons has prepared the way for neglect of the co-ordinates of the light particles.

Another point is that these forces have no appreciable action on the electrons except near the nucleus. Here again, apart from our knowledge of nuclear forces, the analogy helps us. When once the photon is emitted we do not think of it as under the influence of the system whose rearrangement generated it. If we were to introduce the co-ordinates of the β particles they would refer to points near the nucleus. All co-ordinates used are thus those of the nucleus.

From this point the work proceeds by use of methods from the quantum theory of radiation: that is to say, the theory of the emission of photons. A new feature is the introduction of a constant denoted by g, which appears because of our ignorance of the intensity of the interaction. We can appreciate the need for it by thinking of the force between two charges. The law is the inverse square law, but we do not write $F=1/r^2$. Instead of this we have $F=qq'/r^2$, the intensity being determined by q and q', which we call the charges. In Fermi's theory g is not of the dimensions of a charge because he introduces it in a different way, but other writers have introduced it in accordance with this simple idea. The calculation gives the probability of the occurrence, P, of a β particle with energy E. A curve can be plotted to represent this (see figure 2).

The general feature is as shown. The experimental curve ends at the maximum horizontally. On examining the theoretical result it appears that this requires a very small mass for the neutrino, and, indeed. we usually accept the view that its mass is zero.

The disintegration constant is calculated from

$$\lambda = \int P dE.$$

From this we find

$$\lambda \sim g^2 E^5 \left(\frac{2\pi}{hc}\right)^7 c.$$

To see that λ is the constant usually defined by the equation

$$dN = -\lambda N\, dt,$$

let the number of radioactive atoms be N. The number of particles emitted with the energy range E to $E+dE$ is by definition of P measured by $PNdE$ per sec. Thus, for all values of the energy, the number of particles emitted is $N\int PdE$. Thus, with the usual sign convention, the number of particles which have disintegrated in an interval of time dt is denoted by

$$dN = -N\int PdE\, dt.$$

In the case of ThC

$$\lambda = 9\times 10^{-5} \text{ per sec.}$$

Thus

$$g^2 E^5 \left(\frac{2\pi}{hc}\right)^7 c = 9\times 10^{-5}.$$

Since $E = mc^2$, this gives $g \sim 10^{-50}$.

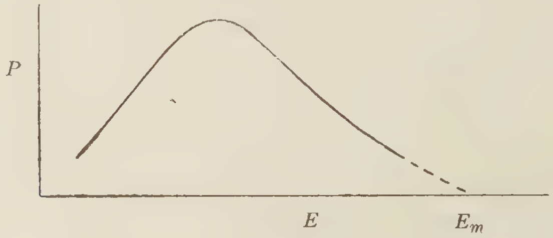


Figure 2.

With this value for g, we can account satisfactorily for λ, and with the zero neutrino mass we can account for the termination of the curve. But the position of the maximum does not come out satisfactorily, and the course of the curve is not sufficiently close to that of the experimental curve. Modifications have been suggested by Konopinski and Uhlenbeck, but they have not altered the position to a degree which makes the theory acceptable. The difficulty is that in this theory we are committed to a calculation of the exchange forces and the nuclear magnetic moment which depend on g. The value of g deduced from the aspect of disintegration is altogether too small for the facts we now have to explain.

From a knowledge of nuclear energies it is known that the order of magnitude of the energy is 10^7 electron volts, i.e. $1{\cdot}59\times 10^{-5}$ erg, but the above value of g gives 10^{-21} erg, i.e. 10^{-9} electron volt.

The order of the disagreement in the case of the magnetic moments is equally disconcerting. From Dirac's theory of the electric charge it appears that a proton should possess a magnetic moment of $he/4\pi Mc$, where M is the mass of the proton. We can speak of this as the nuclear magneton. Since the neutron has no charge, this theory would ascribe zero moment to the neutron. But experimental results which are explained on the basis of the existence of nuclear magnetic moments require 2·9 nuclear magnetons for the proton and 2 of the opposite sign for the neutron.

A suggestion which has been made by Wick is that we can regard Dirac's equation as applicable, but in the interaction between a neutron and proton there is virtually the emission and absorption of an electron and neutrino. In calculating the moment directly from Dirac's equation the effect of this interaction has been neglected. The calculation should be made to take account of the time this electron is present. The result leads to an average value of the nuclear magnetic moment, but owing to the value of g the magnitude is much too small.

Before discussing this point further let us make a digression in order to consider in more detail the character of the interaction between the heavy particles.

§4. INTERACTION BETWEEN A PROTON AND A NEUTRON

Let us consider the interaction between a proton and neutron by which the proton becomes a neutron and the neutron a proton.

We can consider the process in the following way:—

$$P+N=N+e^{+}+n+N=N+P,$$

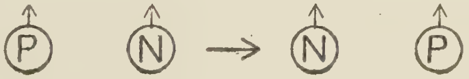
or

$$P+N=P+e^{-}+n+P=N+P.$$

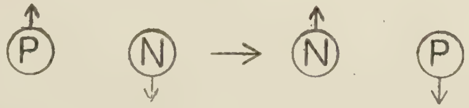
This means that the proton becomes a neutron together with a positron and neutrino and that the two light particles then unite with the neutron to form a proton. We get an interchange of particles.

The question arises whether the proton in its new state as a neutron has the same spin or whether the new proton has the spin of the old one.

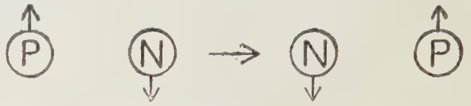
There are two different assumptions in this respect. The first is due to Heisenberg. This postulates that the particle retains its spin in spite of the change. This suggests that spin is a property of space, i.e. it depends on where the particle is, so that in the above interchange P on the left and N on the right have the same spin:



or, if the spins are directed differently,



The other possibility immediately suggests itself. In this case the proton before the change has the same spin as the proton afterwards, and similarly for the neutron. This is *Majorana's hypothesis*:

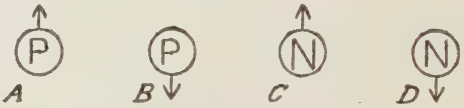


The theoretical treatment takes account of the two possibilities and shows a difference between the two cases.

In the former there is an attraction between the particles for like spins, repulsion for unlike spins. The forces in this case are said to be of the *Heisenberg type.*

In the second case, the forces are said to be of the Majorana type, and they are attractive in both cases.

Suppose we apply this concept to an α particle in order to examine the stability of the structure. In this case there are 2 protons and 2 neutrons, and their spins must be unlike in each pair on account of the exclusion principle:



With Heisenberg forces the only possible changes are *A* with *C* and *B* with *D*, since otherwise we should obtain two similar particle states in one level. This means an association of *A* and *C* and one of *B* and *D* with no force between the pairs. Such a structure does not present the stability associated with the α particle. This is an example of the kind of difficulty that arises if only Heisenberg forces are assumed. The other type leads to an explanation of the stability of the α particle.

It appears from the later types of theory which have been proposed that both types of forces exist and, moreover, an ordinary force in addition.

The method used to obtain a quantitative solution is to apply the theory of perturbations. This implies the assumption that the influence of the emitted particles on the heavy ones can be regarded as small.

§ 5. YUKAWA'S THEORY

Leaving this digression, we return to the difficulties arising from nuclear energies and magnetic moments.

If we take the view that Fermi's theory is on the right lines in explaining the simple facts of β disintegration, the difficulties suggest that it is being forced to do too much in making it explain at the same time the facts about energy and momenta. Can any freedom be obtained for the determination of nuclear forces which Fermi's theory denies us?

This brings us to the next important step in the development of nuclear theory. From time to time in the history of physics, situations of this kind have arisen, and a careful examination has not merely cleared up the difficulties, but has resulted in progress, sometimes dramatically. On one occasion such a situation was associated with the discovery of a new planet. In this case of the failure of Fermi's theory the result has been a new particle. This event in the atomic system has a degree of importance and a touch of drama comparable with the discovery of Uranus in the solar system.

The idea came from Yukawa (1934), and his work is based on the physical ideas of Fermi; but he succeeded in avoiding the disadvantage of Fermi's theory, which is the result of too close an association of the emitted particles and the proton and neutron. In other words, he obtained the freedom denied us in Fermi's theory.

The basis of Yukawa's work is a field theory like that of Maxwell. From it he calculates the energy associated with this field: that part of the energy which is due to the interaction of the proton and neutron associated with emission of particles is $g^2e^{-\lambda r}/r$. g is not the same constant as that in Fermi's theory; its dimensions are different, but it comes into the theory in the same way. λ is another constant of the dimensions 1/length, not to be confused with the disintegration constant.

Neither is determined by the theory, but both have to be fixed by experiment. The experimental results to which an appeal is made are those on the scattering of neutrons by protons and measurements of the mass defect of the deuteron.

If the emitted particle were an emitted electron, λ would be $2\pi \boldsymbol{mc}/\boldsymbol{h}$, where $\boldsymbol{m}$ is the mass of the particle. But this would mean that the rate of fall of the nuclear force with distance would be much too small on account of the small magnitude of $\boldsymbol{m}$. $1/\lambda$ must be of the order of nuclear dimensions, i.e. $\lambda \sim 10^{12}$ to 10^{13}. This means that the mass m must be of the order of 100 to 200 times the mass of the electron. This led to the suggestion that the interaction between proton and neutron must be described in terms of the emission of this heavy electron or *meson*.

At the time of the suggestion no such particle was known, but about two years later, in the study of certain cosmic-ray tracks, it was observed that the momentum and penetrating power could be attributed to a charged particle of this order of mass. It can be accepted that such a particle exists.

The constant g in this theory is of the dimensions of the electric charge and has the value of a few fundamental electric charges.

In this procedure we have approached the question from the side of the nucleus rather than from the side of the emitted particles. The question now is whether these values give the right value, or at any rate the right order, for the disintegration constant.

The theory is that the proton-neutron interaction gives rise to a meson. This is a particle with integral spin, so that the conservation of angular momentum is maintained. The particle takes the energy of the interaction, and the energy principle is also maintained. But the particle has a short life, and disintegrates into an electron and neutrino.

We require the probability of occurrence of an electron (β particle) with energy E. It turns out that the magnitude of the decay constant calculated in this way is of the correct order.

Thus the assumption of the existence of a meson gives a particle whose interaction with the proton or neutron is much greater than that of the electron. This accounts for the large interaction between proton and neutron as well as for the small probability associated with β-ray disintegration.

There remains the question of the nuclear moments. The magnetic moment of the meson is, according to the theory, $\boldsymbol{he}/4\pi mc$, where m is its mass.

On averaging over the time during which this particle may be supposed to exist during the interaction, the order of the nuclear magneton comes out correctly.

The fraction of the time during which the neutron is splitting up into a proton and a negative meson is $\sim 2\pi g^2/\boldsymbol{hc}$. Thus, during this time the meson is contributing to the magnetic moment by an amount

$$\frac{2\pi g^2}{\boldsymbol{hc}} \cdot \frac{\boldsymbol{he}}{4\pi mc} = \frac{2\pi g^2}{\boldsymbol{hc}} \cdot \frac{M}{m} \cdot \left(\frac{\boldsymbol{he}}{4\pi Mc}\right).$$

Now $\frac{2\pi g^2}{\boldsymbol{hc}} \cdot \frac{M}{m} \sim 1$, so that we get a result in agreement with experiment both in sign and order of magnitude.

DISCUSSION

Sir **Owen Richardson**. I had rather hoped that Dr. Flint would have included an account of the present position of the principle of minimum proper time (or its atomicity), which is something that we owe to nobody but himself, and which has always seemed to me a very promising suggestion, to put it at its lowest. Perhaps the reason that it appears to have lost interest (if indeed it has) is due to the circumstance that on the strength of it we prophesied a limit to the atomic numbers of the chemical elements which was shortly afterwards believed to have been exceeded by the products of the neutron bombardments of uranium by Fermi and his school. But these have since been shown to be elements of atomic number about 40 or 50, arising from the fission of the uranium nucleus. So far as I know, there is no evidence that the principle is not true, though there may possibly be scope for improvement in the ways in which it has been derived.

Dr. L. **Pincherle**. The question may be asked whether the particles discovered in cosmic rays with a mass of 100 to 250 times that of the electron are, in fact, to be identified with Yukawa's particles. There has been no universal agreement on this point, but it appears now that the answer should be in the affirmative, as Hamilton, Heitler and Peng succeeded recently in showing that that variant of the meson theory which accounts best for nuclear forces, anomalous magnetic moments, β rays and the quadrupole electric moment of the deuteron is also able to account, on reasonable hypotheses, for all cosmic-ray phenomena.

This form of the meson theory is due to Møller and Rosenfeld, and assumes that there exist two kinds of mesons : one, with spin $\boldsymbol{h}/2\pi$, described by a vector field, and the other, with spin 0, described by a pseudo-scalar field ; both kinds of mesons can be positively or negatively charged, or neutral.

It is assumed that the primary cosmic radiation consists of protons ; these, by collision with nuclear particles, emit mesons, in much the same way as electrons colliding with atoms emit X rays, and the rate of production is so high that nearly all mesons are produced in a top layer of the atmosphere of thickness 20 to 50 cm. H_2O. The variation of the number of mesons with energy, height and geomagnetic latitude is given correctly by this theory. The *vector* mesons have a very short lifetime (10^{-8} sec.) : each disintegrates into a high-energy electron and a neutrino ; these disintegration electrons are the origin of showers, and account satisfactorily for the soft component of cosmic rays. The *pseudo-scalar* mesons have a longer lifetime (10^{-6} sec.) ; their properties correspond to those of the mesons found in cosmic-ray experiments.

Dr. L. **Gilbert**. With reference to the decay of a meson into an electron and a neutron, it was stated by Wynne Williams in a lecture in 1940, soon after he photographed the decay of a meson into an electron, that the mass of the meson went into the kinetic energy of the electron produced and into gamma rays, no mention being made of the neutrino. This accounted for the mass, but apparently the angular momenta or spins were not included, and the neutrino is a necessary postulate for complete conservation of energy.

Mr. C. E. R. Bruce. Can Dr. Flint tell us in what form the energy is liberated when the meson breaks up into β particles and neutrino ? Is it as kinetic energy of the electron entirely, or are γ rays emitted at the same time ?

In the nuclear reactions forming the Bethe cycle in stars, what form does the energy take initially ?

Prof. H. Dingle. The reply to Mr. Bruce's question is that, according to the Bethe theory, the main process of energy generation inside a star is the building up of helium nuclei (α particles) from hydrogen nuclei (protons) by a series of steps in which isotopes of carbon, nitrogen and oxygen play the part of catalysts. The energy released in the process is emitted in the form of high-energy photons and positive β particles, which in the course of their passage towards the surface of the star are transformed into the radiation which the star emits to space. The net result is that the hydrogen content of the star (originally very high) decreases and the helium content increases, the surplus energy being radiated as starlight.

Author's reply. The position of the principle of minimum proper time has, I think, been made clearer by recent developments. It appeared first in an attempt to understand the place of Schroedinger's equation in the theory of relativity. The statement of the principle is that in the study of the motion of any fundamental charged particle carrying charge e and of rest-mass m, it is impossible to associate an interval of proper time with it less than $\boldsymbol{h}/m.\boldsymbol{c}^2$. The obvious place in which to investigate the consequences of the principle is in the orbits of extra-nuclear electrons. In this case, bearing in mind that in terms of ordinary time the least interval is $\boldsymbol{h}/\boldsymbol{m}.\boldsymbol{c}^2(1-v^2/\boldsymbol{c}^2)^{\frac{1}{2}}$, where v denotes the velocity of the particle, it follows that the number of chemical elements built up on the Rutherford model cannot be greater than $\boldsymbol{hc}/2\sqrt{2}\pi\boldsymbol{e}^2$ or $137/\sqrt{2}$, thus not greater than 96. The relation of this principle to modern theories lies in the analogy made between the emission of particles and the emission of photons. It has been pointed out that in the attempt to understand the fundamental position of Schroedinger's and Dirac's equations in the quantum and relativistic theories, it is necessary to add a new degree of freedom to the fundamental charged particle. This has made it possible to draw an exact analogy between the theory of the photon and the particle. This analogy is essentially that the particle, like the photon, can be represented by a null geodesic. Fermi's analogy, to which reference has been made, is one example of this general result. When this additional degree of freedom is taken into account it is found to appear very simply in all existing theories, and by means of it all field theories so far examined can be deduced from a very simple hypothesis in close analogy with well-known theories. It is a familiar fact that in electrical-circuit theory a large class of phenomena can be described by the assumption that the dependence upon time is contained only in the factor $\exp(2\pi jt/T)$, where T is the period. The time appears in many equations merely as the period T. In nuclear field theories the additional degree of freedom appears in the factor $\exp(2\pi j\chi/l)$, where l denotes a fundamental length. Only integral multiples of l appear in the theory. The fact that the particle is to be treated in exact analogy with a photon means that in an electromagnetic field it describes a null geodesic in the continuum of the five co-ordinates or degrees of freedom. This gives the value $\boldsymbol{h}/\boldsymbol{mc}$ to l, where m is the rest mass of the particle. The fact that only integral multiples of l appear in the theory has the consequence that the least proper-time considered in the existing theories is $\boldsymbol{h}/\boldsymbol{mc}^2$. This is only one example of the consequences associated with the introduction of the new degree of freedom. A less direct one is that within the framework of existing theories it is impossible, without running counter to the fundamental postulates, to speak of unlike charged particles within a region of dimensions $\boldsymbol{e}^2/\boldsymbol{mc}^2$, where $\boldsymbol{e}$ is their charge and $\boldsymbol{m}$ their mass. This means that electrons and protons cannot occupy the nucleus, and it also means that if any phenomenon is to be described in terms of an interaction at a distance of 10^{-13} cm. between two charges of unlike sign, as in the case of an electron and atomic nucleus, that electron cannot be associated with its ordinary mass. It turns out by a calculation based on these principles that the mass must be of the order of 100 times that of an ordinary electron. One further consequence is that the theory shows that electric charge is quantized, that is to say, it cannot appear except as integral multiples of a fundamental unit. It seems, therefore, that the principle of minimum proper time takes its place amongst a number of fundamental consequences derived from the analogy drawn between photons and particles. We can say that in the framework of existing theories it is not possible to consider the building up of atoms on the Bohr-Rutherford model, or, indeed, on the basis of modern quantum theory, beyond the number 96 without doing violence to fundamental principles on which the model and the theory are based.

In reply to Mr. Bruce, the energy liberated in the disintegration of the meson is, so far as is known, located entirely in the kinetic energy of the β particle and neutrino, and in their rest masses.

THE SPECTRUM OF NO: ROTATIONAL ANALYSIS OF EPSILON BANDS AND NEW OBSERVATIONS ON THE BETA AND DELTA BAND-SYSTEMS

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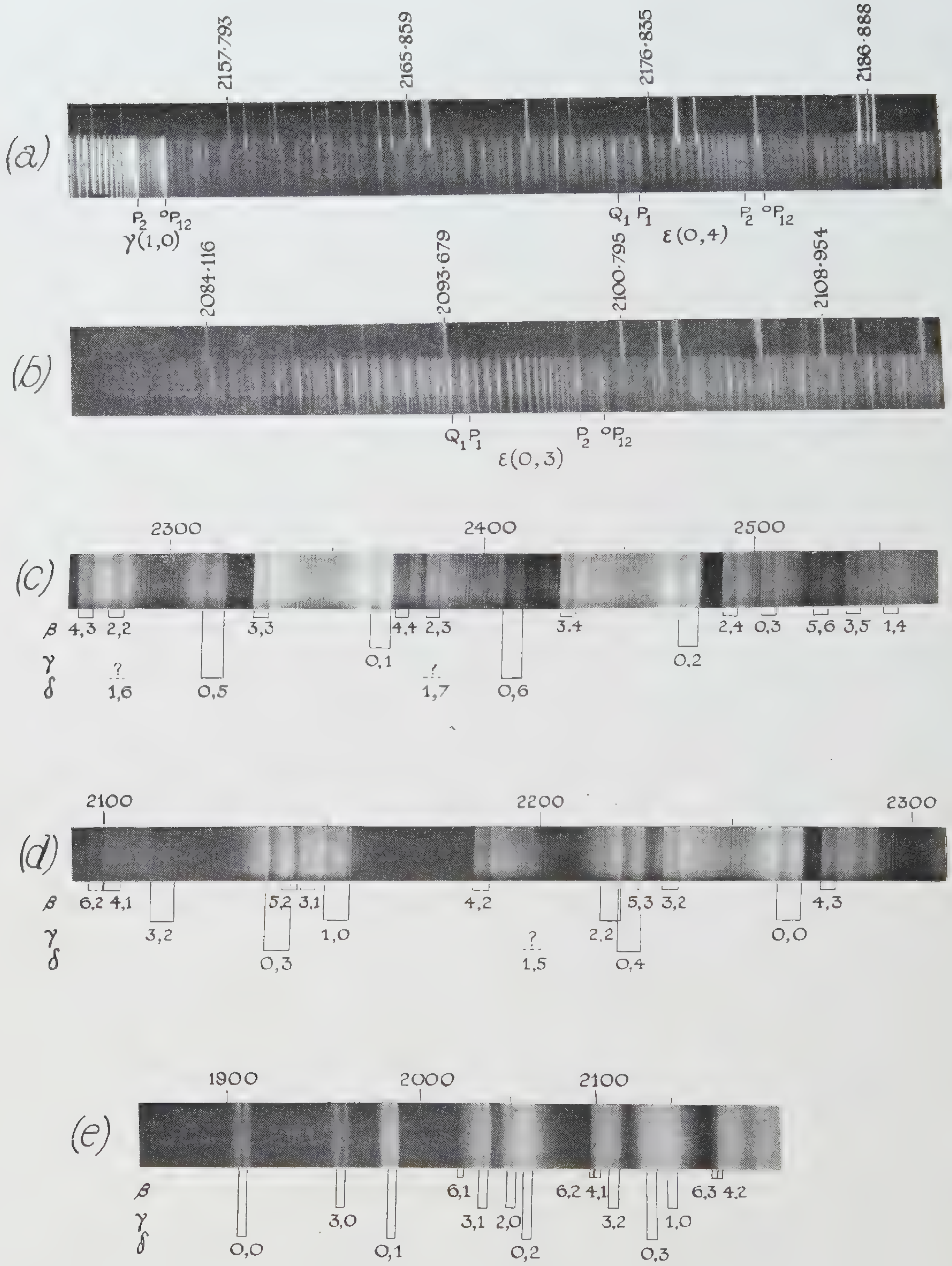
MS. received 18 *January* 1944

ABSTRACT. A rotational analysis has been made for the (0,4) and (0,3) bands of the ϵ system of nitric oxide. Rotational constants have been evaluated and it has been shown from consideration of the defect (due to Λ doubling) between *P*, *Q* and *R* combinations that the initial electronic state is of type $^2\Sigma^+$. Potential-energy curves for the known electronic states of NO are shown. Some observations have also been made on the excitation of the β and δ systems of NO in the nitrogen afterglow. Bands of the β system with $v'=5$ and 6 have been obtained in emission. The energy of dissociation of NO and supposed predissociations in the spectrum are discussed. Flory and Johnston's interpretation of the photodissociation of NO by Hg 1832 A. appears to be incompatible with the present observations on the spectrum.

§ 1. INTRODUCTION

In a recent paper (Gaydon, 1944a) it has been shown that the ϵ band-system of NO appears readily in emission in an ordinary uncondensed discharge through air, and that it is distinct from the γ system. It is clear from the appearance of the bands that the ϵ system corresponds to a transition from a $^2\Sigma$ state to the ground state of NO, which is $^2\Pi$. It was not, however, known whether the upper state was $^2\Sigma^+$ or $^2\Sigma^-$. In order to apply the non-crossing rule to the potential-energy curves of the various electronic states of NO and to discuss the probable value of the dissociation energy of this molecule, it appeared desirable to obtain further evidence about the nature of the initial state of the ϵ bands and to evaluate the rotational constants.

The rotational structure of two bands of the ϵ system has therefore been examined. To determine whether the upper state is $^2\Sigma^+$ or $^2\Sigma^-$ it is necessary to find the sign of the "defect" (due to Λ doubling in the $^2\Pi$ state) between the rotational-term differences obtained from combinations between lines of the



(*a*) and (*b*) Uncondensed discharge through air. E.1 spectrograph. Exposure 15 min. and 30 min. respectively. Iron-arc comparison above.

(*c*) and (*d*) Nitrogen afterglow. E.2 spectrograph. Exposure 5 hours.

(*e*) Nitrogen afterglow. E.3 spectrograph. Exposure 2½ hours.

P and *Q* branches and between lines of the *Q* and *R* branches, and to compare this with the sign of the "defect" obtained from the γ bands which are known to arise from a $^2\Sigma^+$ initial level.

§ 2. EXPERIMENTAL

To excite the spectrum, an ordinary transformer discharge through air at reduced pressure was used, a water-cooled discharge tube of the type described by Hunter and Pearse (1936) being employed. The spectrum was photographed with a large quartz instrument (Hilger E.1) giving a dispersion of 1·6 A./mm. in the required region. This dispersion is a little less than that used by Guillery (1927) for the study of the γ system, but the definition of most of the plates obtained in this investigation was very good, and the resolving power appears to be at least equal to, and probably a little better than, that obtained by Guillery. Ultra-violet sensitive plates (Ilford Q II and Q I) were used, and for some of the work a fine-grain borax developer was employed. Exposure times ranged from 5 to 60 min. An iron-arc comparison spectrum was used.

Spectrograms of the two bands studied, the (0,4) at 2182 A. and the (0,3) at 2099 A., are reproduced in the plate (strips (*a*) and (*b*)). Measurements made from lightly and heavily exposed plates were averaged. Lines were resolved down to about 0·6 cm.$^{-1}$, and comparison of measurements from different plates indicates that the probable error of measurements of unblended lines is about 0·1 cm.$^{-1}$.

§ 3. ROTATIONAL ANALYSIS

The bands of the ϵ system show eight branches, two strong and two weak to each sub-band. Their structure is very similar to that of the bands of the γ system. Rotational analyses of a number of bands of the γ system have been carried out by Guillery (1927) and Schmid (1928, 1930 a). Their work was done during a period of rapid development in the theory of band spectra, and their notation, both for branches and for rotational quantum numbers, differs from that which is now generally in use. The older notation was also used by the author (1944 a) when referring to the band heads of the two systems, but for the purpose of the rotational analysis it is now necessary to use the modern notation. To facilitate comparison of the present rotational analysis of the ϵ bands with that of the γ bands made by Guillery, the two notations are set out below, lines with final quantum number $J = 6\frac{1}{2}$ being taken as an example (see also figure 1).

Present notation	$^{O}P_{12}(6\frac{1}{2})$	$P_2(6\frac{1}{2})$ and $^{P}Q_{12}(6\frac{1}{2})$ (unresolved)	$Q_2(6\frac{1}{2})$ and $^{Q}R_{12}(6\frac{1}{2})$ (unresolved)	$R_2(6\frac{1}{2})$
Guillery's notation	$P_1(6)$	$Q_1(7)$	$R_1(8)$	$R_1'(9)$
Present notation	$P_1(6\frac{1}{2})$	$Q_1(6\frac{1}{2})$ and $^{Q}P_{21}(6\frac{1}{2})$ (unresolved)	$R_1(6\frac{1}{2})$ and $^{R}Q_{21}(6\frac{1}{2})$ (unresolved)	$^{S}R_{21}(6\frac{1}{2})$
Guillery's notation	$P_2(6)$	$Q_2(7)$	$R_2(8)$	$R_2'(9)$

The full analysis of the (0,3) and (0,4) bands has been completed without difficulty. The spin splitting in the initial $^2\Sigma$ state is negligibly small and there is no evidence of resolution of the satellite branches $^{P}Q_{12}$, etc., from the main branches P_2, etc. The Λ doubling, which is small but not negligible, will be discussed in the next section.

For the (0,3) band a high proportion of the lines in the region, including all strong lines, has been assigned to the (0,3) band, and the few weak lines which are not accounted for are readily explained as being due to the "tail" of the (3,2) γ band. For this band the accuracy of the measurements is rather limited by the poor iron standards below 2100 A., and there is also a good deal of overlapping of the P_2 and Q_2 branches, so that, in order to economize space, details of this band are omitted in favour of the (0,4) band.

Full measurements of all lines in the region of the (0,4) band are listed in table 1. Unresolved lines are bracketed, and poor or uncertain assignments are enclosed in parentheses. Intensities are visual estimates on an arbitrary scale of 1 to 10. There are a number of lines at the head and tail of the band which are unclassified. Those at the head are no doubt due to the tail of the

Table 1. Intensities, wave-numbers and assignments of rotational quantum number J to the branches of the (0,4) ϵ band of NO

I	ν	$^{O}P_{12}$	P_2 and $^{P}Q_{12}$	Q_2 and $^{Q}R_{12}$	R_2	P_1	Q_1 and $^{Q}P_{21}$	R_1 and $^{R}Q_{21}$	$^{S}R_{21}$
7	45816·3	H							
4	17·0	9½							
7	18·3	10½							
5	19·45								
4	21·2								
6	22·7	12½							
5	23·7								
6	25·95	13½							
2d	27·4								
4	30·15	14½							
6	31·2								
10	35·35	15½	H						
4	36·8		4½						
6	38·5		5½						
2	40·1	16½							
8d	40·8		6½						
6	43·9		7½						
4	45·25			(1½)					
4	47·0								
9	47·9		8½	(2½)					
9	48·4								
9	51·9			(3½)					
10	52·6	18½	9½						
6	56·65			4½					
10	57·75		10½						
3	60·7	19½							
10	62·7			5½					
10	63·6		11½						
2	66·0								
9	68·8			6½					
9	70·25		12½						
8d	71·8								
5	75·25								
10	75·9			7½					
10	77·65	21½	13½						
2	80·3								
8	83·9			8½					

Table 1 (*continued*)

I	ν	$^OP_{12}$	P_2 and $^PQ_{12}$	Q_2 and $^QR_{12}$	R_2	P_1	Q_1 and $^QP_{21}$	R_1 and $^RQ_{21}$	$^SR_{21}$
8	45885·6		14½						
1	87·6	22½							
1	88·2								
8	90·55				(5½)				
8	92·35			9½					
8	94·3		15½						
5	95·4								
3d	97·8								
2	45900·65				6½				
10	01·5			10½					
10	03·65		16½						
2	07·95								
9	11·5			11½	7½				
9	13·7		17½						
6	16·7								
6	17·8								
5	20·9	(25½)							
10	22·0			12½					
4	23·4				8½				
8	24·45		18½						
2	26·4								
2d	29·65								
9	33·25			13½					
5	34·6								
9	36·0		19½		9½				
7d	37·7					H			
5	38·6					8½, 5½			
2d	39·8					9½			
4	41·9					10½			
2	44·0								
9	45·2			14½		11½			
1	46·55								
9	48·4		20½						
7	48·9				10½	12½			
2	52·0								
3	53·1					13½			
3d	54·65						3½		
3	56·55						4½		
10	58·1			15½		14½			
6	58·9						5½		
6	60·7								
7	61·8		(21½)				6½		
3	62·85				11½				
6	64·55					15½			
7	65·7						7½		
10	70·3						8½		
10	71·05			(16½)		16½			
6	74·8								
7d	75·5		22½				9½		
4	76·2							4½	
4	78·0				12½				
6	78·7					17½			
7	81·8						10½		
4	82·8							5½	

Table 1 (*continued*)

I	ν	$^{O}P_{12}$	P_2 and $^{P}Q_{12}$	Q_2 and $^{Q}R_{12}$	R_2	P_1	Q_1 and $^{Q}P_{21}$	R_1 and $^{R}Q_{21}$	$^{S}R_{21}$
9	45985·3			17½					
3	87·05					18½			
9	88·75						11½		
7	89·65		23½					6½	
4	93·1				13½				
8	96·3					(19½)	12½		
4	97·6							7½	
9	46000·0			18½					
3d	02·55								
8d	04·5		24½				13½		
8	05·85					(20½)		8½	
5d	08·85				14½				
2d	10·1								5½
9	13·95						14½		
10	15·6			19½				9½	
5	16·35					21½			
4	18·7								
5	19·7		25½						
1	21·3								6½
8	23·85						15½		
8d	25·55				15½			10½	
4	27·75					22½			
7	31·6			20½					
3	33·2								7½
7	34·6						16½		
3	35·5		26½						
7	36·45							11½	
5	38·95								
3	39·6					23½			
3	43·0				16½				
3	43·9								
8	46·0						17½		8½
10d	48·35			21½				12½	
2	51·0								
5d	53·1		27½			(24½)			
3	57·5								
8	58·2						18½		
4	59·2								9½
9	60·65				17½			13½	
7	66·0			22½					
2	66·6					25½			
9d	71·2		28½				19½		
8	73·6							14½	10½
4d	76·9								
4	79·5				18½				
3	80·7					26½			
9	84·35			23½					
9	84·8						20½		
6	87·7							15½	
3	88·1								11½
1d	89·3		29½						
5	94·9								
4	95·4					27½			

Table 1 (*continued*)

I	ν	$^{O}P_{12}$	P_2 and $^{P}Q_{12}$	Q_2 and $^{Q}R_{12}$	R_2	P_1	Q_1 and $^{Q}P_{21}$	R_1 and $^{R}Q_{21}$	$^{S}R_{21}$
8	46099·45				19½		21½		
7	99·9								
8	46102·4							16½	
8	03·3			24½					12½
1	08·8		30½						
2	11·7					28½			
7	13·55								
7	14·8						22½		
7	17·75							17½	
5	18·9				20½				
1	20·1								13½
8	22·8			25½					
1d	28·25					29½			
1d	28·7		31½						
6	31·0						23½		
5	34·15							18½	
3	37·35								14½
3	38·7								
3	39·45				21½				
6	43·3			26½					
1d	45·5					30½			
6	47·6						24½		
7	49·2		(32½)						
7	50·95							19½	
1d	55·0								15½
6	60·3								
6	61·1				22½				
5	64·35			27½		(31½)			
6	65·1						25½		
5	66·0								
6	68·5							20½	
1	70·65		33½						
3	73·5								16½
3d	75·7								
3	79·1								
2	82·65					32½			
9	83·4				23½		26½		
8	86·15			28½					
8	87·05							21½	
2	93·0								17½
5	96·8								
1	98·0								
4	46200·0								
1	01·5					33½			
5	02·6						27½		
7	06·3				24½			22½	
7	08·4			29½					
4	11·4								
1	12·9								18½
7	16·45								
7	22·3						28½		
7	26·35							23½	
2d	30·0				25½				

Table 1 (*continued*)

I	ν	${}^{O}P_{12}$	P_2 and ${}^{P}Q_{12}$	Q_2 and ${}^{Q}R_{12}$	R_2	P_1	Q_1 and ${}^{Q}P_{21}$	R_1 and ${}^{R}Q_{21}$	${}^{S}R_{21}$
7	46231·9			30½					
6	32·2								
1d	34·35								19½
3d	42·8						29½		
3d	43·1								
7	46·2								
7	47·0							24½	
7d	48·2								
3	53·9				26½				
4	55·65			31½					20½
1	58·15								
7	63·2								
7	63·95						(30½)		
6	65·95								
6	68·4							25½	
1d	72·6								
9d	78·8				27½				21½
9d	79·8			32½					
1d	83·3								
4	86·3						31½		
4	88·25								
5	90·8							26½	
5	94·0								
7d	98·9								
1	46301·25								22½
5d	04·65			33½	28½				
3	05·6								
2	07·1								
6	08·25								
1	08·8						32½		
5	12·3								
4	13·9							27½	
6	22·9								
1	28·05								
5	30·7			34½	29½				
3	31·55								
4	32·45						33½		
5d	36·35	Probably head of (1,5) ϵ band							

d = diffuse or broad lines. H = head of branch.
Unresolved lines are bracketed together.

(3,3) γ band. The origin of the unassigned lines in the region of the tail of the (0,4) band is uncertain. A number of lines can be fitted into a rather erratic branch which is degraded to the red (46322·9, 308·25, 294·0, 278·8, 263·2, 248·2, 232·2, 216·45, 200·0, etc.); this *might* be due to the (6,15) Lyman-Birge-Hopfield band of N_2 which has been observed by Appleyard (1932). There is no definite sign of the (4,4) γ band, which should lie in the same region as the (0,4) ϵ band. The intensity distribution (Gaydon, 1944 a) would not suggest an appreciable intensity for this γ band.

The rotational constants for the upper state come out at

$$B_0' = 1{\cdot}99_2 \text{ cm.}^{-1} \qquad D_0' = 6 \times 10^{-6} \text{ cm.}^{-1}$$

The origins of the two sub-bands of the (0,3) and (0,4) bands are calculated to lie at 47748·3, 47629·3; 45956·1, 45837·7 cm^{-1} respectively. Combining these values with data from the analysis of the γ bands, and using $\omega_e'=2327$, $x_e\omega_e'=23$, we obtain

$$\nu_0=53292{\cdot}6\ \text{cm}^{-1} \qquad \nu_e=53083\ \text{cm}^{-1}$$

§ 4. THE Λ DOUBLING

The twelve branches expected for a $^2\Sigma^+$ to $^2\Pi$ transition, where the $^2\Pi$ state approximates to Hund's case *a*, are indicated in figure 1, which is based on that given by Jevons (1932). In this diagram the spin splitting in the $^2\Sigma$ state and the Λ doubling of the rotational levels of the $^2\Pi$ state are exaggerated, while the spin splitting of the $^2\Pi$ (i.e. the separation between $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$) is reduced for convenience. For both the ϵ and γ bands of NO, the spin splitting in the $^2\Sigma$ state is negligibly small, and the Λ doubling is also small, and was ignored by Guillery and by Schmid. Examination of Guillery's measurements shows, however, that it is not negligible; Schmid's results are rather marred by multiple use of lines.

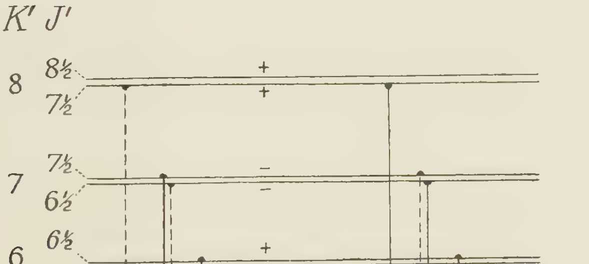


Figure 1. Branches in a $^2\Sigma^+\rightarrow{}^2\Pi$ (case *a*) transition.

It will be seen from the figure that, concentrating on the combinations giving the rotational term differences in the $^2\Pi_{1/2}$ state,

$$\underbrace{Q_1(J)-P_1(J+1)}_{(a)}=\underbrace{{}^SR_{21}(J)-R_1(J+1)}_{(b)}=\underbrace{R_1(J)-Q_1(J+1)}_{(c)}+\Lambda(J)+\Lambda(J+1),$$

where $\Lambda(J)$ and $\Lambda(J+1)$ are the Λ doublings in the J and $J+1$ levels of the $^2\Pi_{1/2}$ state, the equality between (*a*) and the expression including (*c*) is always true; the equality between (*b*) and (*a*) or (*c*) depends on the spin splitting in the $^2\Sigma$ state being negligible. Thus the "defect" between the combinations (*a*) or (*b*) and the combination (*c*) is roughly equal to twice the Λ doubling. Similar relations hold for the $^2\Pi_{3/2}$ state.

Table 2. Rotational term differences and Λ doubling for the $^2\Pi_{1/2}$ state

J	$R_1(J)-Q_1(J+1)$		$Q_1(J)-P_1(J+1)$		$^SR_{21}(J)-R_1(J+1)$		2Λ (average)	
	$\gamma(0,4)$	$\epsilon(0,4)$	$\gamma(0,4)$	$\epsilon(0,4)$	$\gamma(0,4)$	$\epsilon(0,4)$	γ	ϵ
½	(4·8)		(4·4)				(+0·4)	
1½	(7·9)		(8·0)				(−0·1)	
2½	(11·2)		(11·2)				(0·0)	
3½	(14·4)		(14·3)				(+0·1)	
4½	(17·7)	(17·3)	(17·8)				(−0·1)	
5½	20·8	(21·0)	(21·0)	(21·2)		(20·45)	(−0·2)	(−0·07)
6½	24·1	(23·95)	(24·0)	(24·1)		23·7	(+0·1)	(+0·25)
7½	(27·2)	27·3	(27·6)	27·1		27·35	(−0·6)	+0·07
8½	30·4	30·35	(30·3)	(30·5)		(30·4)	(+0·1)	(−0·1)
9½	33·7	(33·8)	33·6	33·6		33·65	+0·1	(+0·17)
10½	37·1	36·8	(37·0)	(36·6)	35·4	(37·15)	+1·7	(−0·07)
11½	40·2	40·15	(39·8)	(39·85)	39·7	(39·75)	+0·5	(+0·35)
12½	43·2	(43·85)	43·1	43·2	43·1	(42·65)	+0·1	(+1·0)
13½	46·6	46·7	46·6	(46·4)	46·7	46·5	−0·05	+0·2
14½	49·6	49·75	49·5	49·4	50·1	49·65	−0·2	+0·23
15½	52·9	53·1	(53·0)	(52·8)	53·0	52·6	−0·1	+0·5
16½	56·0	56·4	55·7	55·9	55·7	55·75	+0·3	+0·67
17½	59·7	59·55	59·0	58·95	59·1	(58·85)	+0·65	+0·6
18½	62·7	62·95	62·2	(61·9)	62·4	61·95	+0·4	+1·0
19½	66·0	66·15	(65·5)	(65·35)	65·8	65·85	+0·2	+0·3
20½	69·0	69·05	68·2	(68·45)	68·8	68·6	+0·5	+0·45
21½	72·2	72·25	71·7	71·7	(71·4)*	(72·5)	+0·5	+0·55
22½	75·7	75·3	75·0	75·2		74·9	+0·7	+0·35
23½	78·8	78·75	78·3	(77·9)			+0·5	(+0·85)
24½	81·9	81·9	81·3	81·0			+0·6	+0·9
25½	84·9	85·0	84·6	84·4			+0·3	+0·6
26½	88·2	88·2	87·8	88·0			+0·6	+0·4
27½	91·3	91·6	90·8	90·9			+0·5	+0·7
28½	94·7		94·2	94·05			+0·5	
29½	97·7		97·2	(97·3)			+0·5	
30½	100·9		100·5	(99·6)			+0·4	
31½	104·1		103·6	(103·65			+0·5	

* For this difference Guillery's assignment has been amended.

For a $^2\Sigma^-$ upper state the + and − signs attached to the rotational levels of this state will be reversed, so that the transitions indicated in figure 1 will take place to the other Λ components of the rotational levels of the $^2\Pi$ state. This results in the expression on the right, which is

$$R_1(J)-P_1(J+1)+\Lambda(J)+\Lambda(J+1) \text{ for a } {}^2\Sigma^+ \text{ upper state,}$$

being changed to

$$R_1(J)-P_1(J+1)-\Lambda(J)-\Lambda(J+1) \text{ for a } {}^2\Sigma^- \text{ upper state,}$$

Thus, by determining the sign of the "defect" it is possible to say whether the upper state is $^2\Sigma^+$ or $^2\Sigma^-$. In tables 2 and 3 the various combinations and "defects" for both $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ are set out for the (0,4) γ band and for the (0,4) ϵ band, the values for the γ band being taken from those given by Guillery (1927). In these tables, combinations depending on lines which are judged to be badly blended are bracketed. The defect, headed 2Λ, is the combination (*c*) less the average of the combinations (*a*) and (*b*); where one of these combinations involves blended lines, this is ignored in preference to the unblended combination.

Table 3. Rotational term differences and Λ doubling for the $^2\Pi_{3/2}$ state

J	$Q_2(J)-P_2(J+1)$		$R_2(J)-Q_2(J+1)$		$P_2(J)-{}^OP_{12}(J+1)$		2Λ (average)	
	γ (0,4)	ϵ (0,4)	γ (0,4)	ϵ (0,4)	γ (0,4)	ϵ (0,4)	γ	ϵ
1½	(8·5)				(8·6)		(−0·1)	
2½	(11·3)		(11·3)		(11·7)		(−0·2)	
3½	(15·2)	(15·1)	(14·5)		(15·3)		(+0·7)	
4½	18·2	18·15	18·3		18·0		+0·05	
5½	21·4	21·9	21·1	(21·75)	21·5		+0·1	(+0·15)
6½	24·9	24·9	24·6	24·75		(24·5)	+0·3	+0·15
7½	28·3	28·0	(27·1)	(27·6)	27·7	(27·6)	+0·6	(+0·4)
8½	31·6	31·3	(31·0)	31·05		30·9	(+0·6)	+0·32
9½	34·8	34·6	34·5	(34·5)	34·4	34·6	+0·35	0·0
10½	38·0	37·9	(37·3)	(37·4)	37·7		+0·3	(+0·5)
11½	41·3	41·25	(41·1)	40·85	41·1	40·9	+0·2	+0·37
12½	44·5	44·35	43·9	44·75	44·3	44·3	+0·4	−0·17
13½	48·0	47·65	47·3	47·9	47·6	47·5	+0·7	−0·05
14½	51·3	50·9	50·9	(50·75)	50·7	(50·25)	+0·5	(+0·4)
15½	54·3	54·45	54·0		54·4	54·2	+0·1	+0·25
16½	(57·8)		57·4	57·7	57·4		(+0·4)	
17½	60·9	60·85	60·6	(60·65)	(60·7)	(61·1)	+0·3	(−0·02)
18½	64·2	64·0	(64·0)	63·9	(64·1)	63·75	(+0·15)	+0·17
19½	67·3	67·2	(67·4)	(67·85)	67·1		+0·2	(−0·65)
20½	70·7	(69·8)	(70·2)	70·55	70·7	(71·75)	0·0	(−0·75)
21½	73·7	(72·85)	73·6	73·45	73·8	(74·2)	0·0	(−0·6)
22½	77·1	76·35	76·9	(76·75)	77·0		+0·15	(−0·4)
23½	80·5	(79·85)	(80·1)	(80·1)	80·1		+0·4	(−0·25)
24½	(83·5)	83·6	83·5	83·5	83·3		(+0·1)	+0·1
25½	86·8	87·3	86·6	86·7	86·4		+0·3	+0·5
26½	89·8	90·2	*	89·55				+0·75
27½	93·2	(93·15)	(93·2)	(92·65)			(0·0)	(+0·5)
28½	96·0	96·85	(96·2)	(96·25)			(−0·2)	(+0·65)
29½	(99·4)	(99·6)	(98·8)	(98·8)			(+0·6)	(+0·8)
30½	102·7	(103·2)		(101·6)			(+1·1)	

* There appears to be a misprint in Guillery's value.

Examination of table 2 shows that for the $^2\Pi_{1/2}$ state the doubling below $J=15\frac{1}{2}$ is small and the defect is dominated by the experimental error, but that at higher J values the doubling becomes appreciable and the defect assumes a quite definite positive value for both the γ and ϵ bands. This shows that for both the γ and ϵ systems the initial state is $^2\Sigma^+$. For the $^2\Pi_{3/2}$ state it is also clear that at high J values the sign of the defect tends to become positive, but in this case the doubling is smaller, and rather a high proportion of the lines of the $^2\Pi_{3/2}$ sub-band are blended with stronger lines of the $^2\Pi_{1/2}$ sub-band, so that the results are less decisive.

§ 5. THE POTENTIAL-ENERGY CURVES

The potential-energy curves for all the known electronic states of NO are plotted in figure 2. For the ground X $^2\Pi$ state a Morse function has been used, taking the dissociation limit at 60 000 cm.$^{-1}$, which approximates to its extrapolated value. For the upper states, potential functions of the type assumed by Dunham (1932) have been used,

$$U(\xi)=a_0\xi^2(1+a_1\xi+a_2\xi^2+\dots),$$

where U is the potential energy and $\xi=(r-r_e)/r_e$, r being the internuclear distance

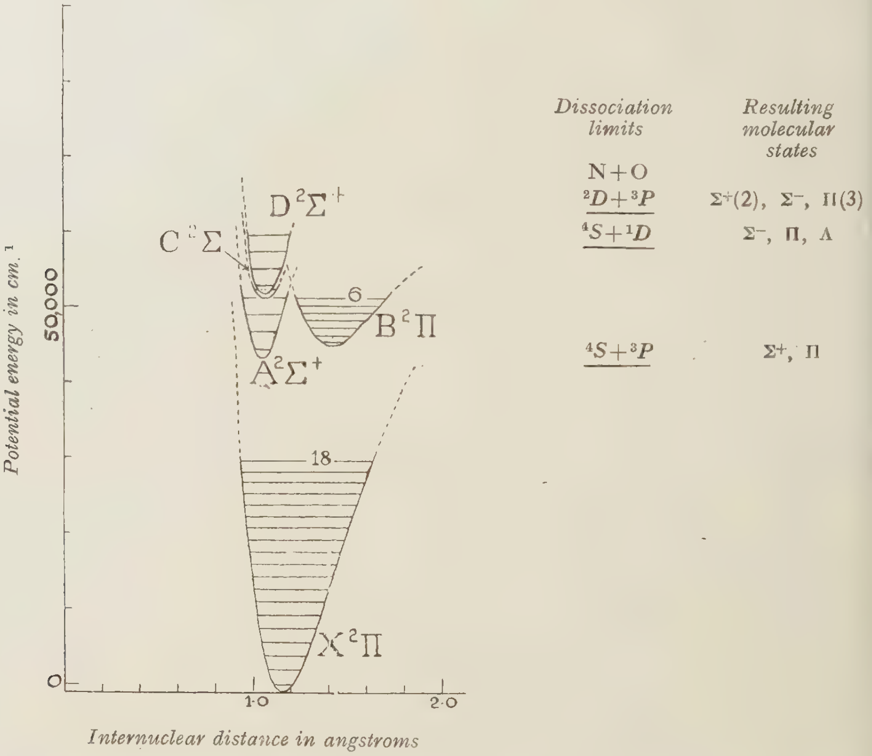


Figure 2 Potential-energy curves for the electronic states of NO. Dissociation limits are inserted on the assumption, probably incorrect, that $D(\mathrm{NO})=42\,700$ cm.$^{-1}$.

and r_e its equilibrium value. Within the accuracy required to plot the curves for the present purpose,

$$a_0=\omega_e^2/4B_e,\quad a_1=-\left(1+\frac{\alpha\omega_e}{6B_e^2}\right)\quad\text{and}\quad a_2=\frac{5}{4}a_1^2-\frac{2x_e\omega_e}{3B_e}.$$

Values of the vibrational and rotational constants ω_e, $x_e\omega_e$, B_e and α for the A $^2\Sigma^+$ upper level of the γ bands and for the B $^2\Pi$ upper level of the β system are taken from Schmid (1930 a), while those for the C $^2\Sigma$ upper level of the δ system are from Schmid (1930 b), and for the D $^2\Sigma^+$ level of the ϵ system from the author's measurements. The C $^2\Sigma$ state is usually quoted as being Σ^+, but the author is unaware of any evidence to show whether it is Σ^+ or Σ^-; Schmid's rotational analysis of the δ bands is inadequate to show the sign of the defect due to Λ doubling.

Closely similar potential curves have been published by Schmid (1930 a) and Flory and Johnston (1935), but the additional data, now available, for D $^2\Sigma^+$ are included in figure 2. Only certainly known vibrational levels are indicated. Levels of the C state with $v=1$, and probably 2, are indicated by Liefson's work (1926) on the absorption spectrum. The lowest-lying dissociation limits and the molecular states derived from these by applying the Wigner-Witmer correlation rules are indicated. These molecular states should exist with doublet and quartet multiplicities, and, for the lowest products, sextet as well. The limit $^2D+^3P$ also leads to Δ and Φ states.

§6. PREDISSOCIATION, PHOTODISSOCIATION AND THE DISSOCIATION ENERGY

On the assumption that the dissociation energy of N_2 is 7·38 ev., the dissociation energy of NO must be about 42 700 cm.$^{-1}$, which lies just below all the known excited electronic levels of this molecule. This has led to the expectation that these excited levels might show predissociation, and a good deal of "wishful thinking" appears to have resulted. It has already been shown that Herzberg and Mundie's suggestion that the ϵ bands arise from predissociated levels of the A $^2\Sigma^+$ state is untenable. Kaplan (1931) suggested that the absence in emission of β bands with $v'>4$ was due to predissociation setting in at this point, and this statement has been quoted by Herzberg and Mundie and by Flory and Johnston. Actually, as shown in the next section, bands with $v'=5$ have long been known, and there is no difficulty in obtaining bands with $v'=6$ in emission.

For the C $^2\Sigma$ state, only bands with $v=0$ have been observed with certainty in emission, although bands with $v=1$, and probably 2, are known in absorption. It has therefore been suggested that levels above $v=0$ may be predissociated. Flory and Johnston (1935) have studied the photodissociation of NO and concluded that the dissociation which they observed was due to absorption of Hg λ1832 in the (1,0) δ band, which, in consequence of the supposed predissociation, resulted in immediate dissociation of the molecule. They show a diagram of the potential-energy curves with a repulsive curve started from the lowest dissociation products crossing and predissociating B $^2\Pi$ at $v=4$, A $^2\Sigma^+$ at 4, C $^2\Sigma$ below 1 and also cutting D below $v=1$. With the new knowledge that B $^2\Pi$ is not predissociated below $v=6$, and that state D is of type $^2\Sigma^+$, and is not predissociated below $v=2$, it becomes clear that their explanation of the photodissociation is certainly incorrect in detail and may be altogether wide of the mark. From inspection of the potential curves it would clearly be very difficult to imagine any repulsive curve which could predissociate C $^2\Sigma$ (whether it be Σ^+ or Σ^-) below $v=1$ without also causing predissociation in D $^2\Sigma^+$ (the curve for which lies very close indeed to that for C) and B $^2\Pi$. It may be noted that Flory and Johnston's observations are at variance with those of Macdonald (1928).

The importance of observing the non-crossing rule, that potential curves of molecular states of the same electronic species never cross, when deriving dissociation energies, has been stressed by Gaydon and Penney (1942), who have given reasons for doubting the low value of 7·38 ev. for $D(N_2)$. For NO there appears to be some difficulty, on the basis of $D(\mathrm{NO}) = 42\,700$ cm.$^{-1}$, in correlating the known potential curves with the molecular states arising from the various dissociation products. The lowest products, $\mathrm{N}(^4S)+\mathrm{O}(^3P)$, lead to $^2\Sigma^+$, $^2\Pi$, $^4\Sigma^+$, $^4\Pi$, $^6\Sigma^+$ and $^6\Pi$ molecular states. Of these, the $^2\Sigma^+$ must either link up with A $^2\Sigma^+$ or lie entirely below it if the non-crossing rule is to be maintained. If it were to lie below A $^2\Sigma^+$ this would mean that a stable state of NO of low energy has escaped observation, which seems very improbable. If it links up with A $^2\Sigma^+$, then the resulting potential curve would have to possess a very pronounced maximum, of such height and width that there must be no appreciable overlap of the wave-functions of the vibrational levels in the minimum with those of the continuum up to at least $v=3$, an assumption which seems very artificial. The vibrational levels of the ground state extrapolate to about 61 000 cm.$^{-1}$, and those of B $^2\Pi$, which should dissociate to $\mathrm{N}(^4S)+\mathrm{O}(^1D)$, to about 80 000 cm.$^{-1}$. All these facts point to a dissociation energy of between 51 000 and 61 000 cm.$^{-1}$, probably nearer the latter. Thus considerations of the potential-energy curves of NO do not lead to any precise value for $D(\mathrm{NO})$, but do cast suspicion on the low value (42 700 cm.$^{-1}$) at present in use.

§7. EXCITATION OF THE β, γ AND δ SYSTEMS IN THE NITROGEN AFTERGLOW

In the previous section it has been shown that consideration of the potential-energy curves leads to some doubt about the reality of certain previously assumed predissociations in the spectrum of NO. This section describes some additional experimental work on the excitation of the β, γ and δ systems in the nitrogen afterglow.

The afterglow of commercial nitrogen (containing a trace of oxygen) was excited strongly in an L-shaped discharge tube. A mildly condensed discharge from a powerful induction coil was maintained in one arm of the tube and the afterglow was observed end-on in the other arm; the gas, at a pressure of a few mm., was pumped continuously through the tube. Heavy exposures were made with small (E. 3) and medium size (E. 2) quartz spectrographs. Ilford Q II plates were used.

Previous observations of the β system in the nitrogen afterglow have been made by Johnson and Jenkins (1926), Jenkins, Barton and Mulliken (1927), and Schmid (1930 a). Johnson and Jenkins' measurements include three bands with first heads at 3662·4, 3355·2 and 2523·2 A.; these are undoubtedly the (5,13), (5,12) and (5,6) bands, which lie not on the main Franck-Condon parabola but on a second, subsidiary, parabola. All these earlier observations appear to have been limited at the short-wave end by failing plate-sensitivity. On the author's spectrograms (see strips (*c*), (*d*) and (*e*) of the plate) the short-wave end is well developed, and a number of new bands have been recorded. These are listed in table 4, intensities being visual estimates on a scale of 10 for the strongest bands of the system. The (4,2) and (4,3) bands are quite strong, and the (5,2), (5,3) and (5,6) bands are of fair intensity and are easily visible on the E. 2 spectrograms. The (6,2) and (6,3) are also faintly but definitely visible on the E. 2 negatives, though they do not show up well in the reproduction. The (6,1) and (6,2) bands are, however, visible on the E. 3 plate and are quite strong on some heavily exposed plates taken with a very wide slit. All the new bands at the short-wave end lie on the main Franck-Condon parabola. The intensity distribution appears quite normal. There is thus no evidence for predissociation of the B $^2\Pi$ state below $v'=6$.

The $v'=0$ progression of the δ system (including the new (0,6) band at 2414·6, 2407·6 A.) appears strongly in the afterglow. It has not, however, been possible to demonstrate positively the existence of bands with $v'=1$. There is, indeed, a little unassigned band structure approximately in the positions expected for the (1,7), (1,6) and (1,5) bands, and this is indicated in the reproduction by question marks, but it has not been possible to locate heads or give conclusive proof of the reality of these bands. The γ bands were also present in the spectrum of the afterglow, especially at high gas pressure (low pressure strongly favours the δ system), but no bands with $v'>3$ were observed.

Table 4. New bands of the β system

v', v''	λ	I	ν	v', v''	λ	I	ν
6, 1	2018·1	0	49536	5, 3	*m*	2	(44913)
	2021·1		49466		2229·8		44833
6, 2	2096·4	1	47685	3, 2	2232·0	6	44789
	m				2236·1		44707
4, 1	2099·8	2	47608	2, 2	*m*	2	(43786)
	2103·6		47522		2287·6		43701
5, 2	2139·1	3	46733	4, 4	2371·6	1	42152
	2142·8		46653		2376·2		42072
3, 1	2143·5	3	46637	5, 6	2523·6	1	39614
	m				2528·7		39534
6, 3	2179·2	0	45872	3, 5	2536·3	3	39416
	2183·2		45790		2542·3		39323

m = masked by other structures.

It may be noted that all the systems are readily excited up to about the same energy, around 52 000 cm.$^{-1}$ (β, $v'=6$; γ, $v'=3$; δ, $v'=0$). This might be interpreted either as predissociation in all three electronic states at about this energy, or as the limiting energy available for the excitation of NO by active nitrogen. In favour of the latter alternative, it should be noted that the ϵ bands, which are readily obtained in an uncondensed discharge in air, do *not* occur at all in active nitrogen.

§ 8. ACKNOWLEDGMENTS

In conclusion, I should like to express my thanks to Sir Alfred Egerton for his interest in this work, and to the Council of the Royal Society for financial assistance.

[*Note added in proof.* It has now been shown (Gaydon, 1944 b) that the predissociation in the First Positive bands of N_2, on which the value of 7·38 ev. for $D(N_2)$ is based, is capable of a different interpretation which leads to $D(N_2) = 9{\cdot}76$ ev., giving $D(\mathrm{NO}) = 6{\cdot}49$ ev. ($= 52\,500$ cm.$^{-1}$). This is within the range of values (51 000 to 61 000 cm.$^{-1}$) required by the results reported above.

Dr. W. Jevons has kindly called my attention to a recent note by Gerö, Schmid and Szily (1943) in which a rotational analysis of the (0, 2) and (0, 3) ϵ bands of NO, as obtained in *absorption*, is briefly reported. They agree in regarding the ϵ and γ systems as separate and giving $B' = 1{\cdot}99$, compared with the above value of $1{\cdot}99_2$. No details of the analysis or discussion of the nature of the upper electronic state are given.]

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THE DIFFRACTION OF X RAYS BY DISTORTED CRYSTAL AGGREGATES—I

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ABSTRACT. Broadening of the Debye-Scherrer lines in x-ray photographs of cold-worked metals has been attributed (i) to breaking up of the crystals into " crystallites " whose linear dimensions are $\lesssim 10^{-5}$ cm., (ii) to the presence of crystal grains of different lattice parameters, and (iii) to distortion of comparatively large crystal grains. The broadening to be expected on the last hypothesis is worked out approximately. It is found that the " apparent strain " is given by

$$\eta \equiv \beta \cot \theta = 2/\phi_{hkl}(0),$$

where β is the (corrected) integral breadth of the *hkl* reflection, θ is the Bragg angle, and $\phi_{hkl}(e)de$ is the fraction of the crystal for which the tensile strain in the *hkl* direction is between e and $e+de$.

To relate η with the internal stresses requires some approximations. In cubic crystals fairly plausible assumptions lead to the equation

$$\eta^2=A+BH,$$

where A and B are constants involving the elastic moduli and the mean square values of the direct and shear stresses, and $H\equiv(k^2l^2+l^2h^2+h^2k^2)/(h^2+k^2+l^2)^2$. This equation is verified within the rather large experimental error for metal filings and wire. Details of the experimental work will be published elsewhere.

§ 1. INTRODUCTION

LINE-BROADENING in x-ray photographs of cold-worked metals has been the subject of many investigations. Three suggestions have been made as to its origin:

(i) that the metal is broken up into "crystallites" so small (10^{-5} to 10^{-6} cm. in linear dimensions) that diffraction broadening occurs;

(ii) that the metal is broken up into crystals ($\sim 10^{-4}$ cm. in linear dimensions) with different mean lattice parameters; and

(iii) that the broadening is due to distortion of fairly large crystals ($\sim 10^{-4}$ cm. in linear dimensions).

The distinction between the second and third hypotheses is chiefly in the distortion assumed to be present. In the second hypothesis, the only "distortion" is a uniform expansion or contraction of the whole crystal, whereas in the third, non-uniform expansions and contractions, as well as twists and bends, are allowed.

The first hypothesis is found chiefly in the later papers of Wood (1941, 1943), the second is associated with Brindley (1940), and special cases of the third have been treated by Dehlinger (1927), Boas (1937), and others. On the first hypothesis, $\beta\cos\theta/\lambda$ (where β is the corrected integral breadth of the Debye-Scherrer line, θ the Bragg angle and λ the x-ray wave-length) should be independent of θ and λ, and on the second and third hypotheses $\beta\cot\theta$ should be independent of θ and λ. The problem is complicated by the fact that, in addition to the general variation of β with θ, β may vary in a complicated way with the indices of reflection. On the first ("fragmentation") hypothesis, the variation will depend on the shape of the fragments (Patterson, 1939; Waller, 1939; Stokes and Wilson, 1942), but can hardly be very great. On the second hypothesis, at any rate in the simple form stated above, no variation would be expected. On the third ("distortion") hypothesis, the variation would be zero only if the tensile strain were, on the average, independent of crystallographic direction. As, however, even cubic crystals are not elastically isotropic, this would involve a variation of stress with crystallographic direction. On general considerations of static equilibrium it seems more likely that the stress will be, on the average, independent of crystallographic direction. The resulting variation of tensile strain will then produce a variation of $\beta\cot\theta$.

In the present paper certain consequences of the third hypothesis are investigated. In his discussion of line-broadening by small crystals, Jones (1938) found it convenient to introduce a quantity, the "apparent particle size", defined by

$$\epsilon = \lambda/\beta \cos\theta, \qquad \ldots\ldots(1)$$

which is independent of wave-length and angle of reflection, and depends only on the thickness of the crystal measured perpendicular to the reflecting planes (Waller, 1939; Stokes and Wilson, 1942). Similarly, in discussing line-broadening by internal strains, it is convenient to introduce the "apparent tensile strain" defined by

$$\eta = \beta \cot\theta, \qquad \ldots\ldots(2)$$

which is independent of the wave-length and angle of reflection, and, to the approximation to which it has been possible to carry the calculations, depends only on the distribution of tensile strains perpendicular to the reflecting planes. If the fraction of the crystal for which the tensile strain in the *hkl* direction lies between e and $e+de$ is $\phi_{hkl}(e)de$, then (§ 2 below)

$$\eta = 2/\phi_{hkl}(0); \qquad \ldots\ldots(3)$$

i.e., *the apparent strain is twice the integral breadth of the curve giving the distribution of tensile strain in the hkl direction.* It is therefore possible to obtain $\phi_{hkl}(0)$ from measurements of integral breadth. In principle it is possible to obtain the whole curve $\phi_{hkl}(e)$ from photometry of both sharp and broadened lines, but it requires a rather complicated analysis of the photometer curves, involving the numerical evaluation of Fourier transforms.

Thus, for any particular reflection, the consequences of hypotheses (ii) and (iii) are indistinguishable—to the approximation reached it does not matter whether the variation of lattice parameter takes place in a single crystal grain or from grain to grain, each grain having a constant lattice parameter. Hypothesis (iii), however, offers some hope of correlating the variation of η with the mean stresses and the elastic constants of the material. In the present paper the consequences of the assumption that the stresses are statistically isotropic are worked out for two approximations to the stress distribution. Both lead to the result that η is a function of $H \equiv (k^2l^2+l^2h^2+h^2k^2)/(h^2+k^2+l^2)^2$ only. The second approximation seems preferable, and leads to the relation

$$\eta^2 = A + BH, \qquad \ldots\ldots(4)$$

where A and B are constants depending on the elastic constants of the crystal and the mean square values of the direct and shear stresses. This equation is verified within the rather large experimental error for Cu and Cu_3Ni filings and cold-worked Cu wire. The experimental results will be given in detail elsewhere.

§ 2. GENERAL CALCULATION OF THE INTEGRAL BREADTHS

It has been shown (Wilson, 1943) that the apparent particle size of imperfect crystals is given by

$$\epsilon = J_0^{-1} \int_{-\infty}^{+\infty} J_t \, dt, \qquad \ldots\ldots(5)$$

where J_t is the mean value of the product FF^* of the structure amplitudes of two cells separated a distance t in the *hkl* direction. In a distorted crystal the structure amplitude of the unit cell originally at $\mathbf{r}$ will differ from that at the origin for two reasons: the cell is displaced bodily by an amount $\mathbf{u}(\mathbf{r})$, and suffers a rotation of $\frac{1}{2}\nabla \times \mathbf{u}$. The effect of the rotation on the phase of the x rays scattered from the cell is small compared with that of the displacement, and may be neglected in a first approximation. The structure amplitude of the cell at $\mathbf{r}$ for the *hkl* reflection becomes, therefore,

$$F' = F \exp\{-2\pi i \mathbf{h}.\mathbf{u}\}; \qquad \ldots\ldots(6)$$

F is the structure amplitude of a unit cell of the undistorted crystal and $\mathbf{h} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$, where the **b**s are the edges of the unit cell of the reciprocal lattice. The product of the structure amplitudes of two cells separated a distance t in the direction of $\mathbf{h}$ is therefore

$$\begin{aligned} F'F'^* &= FF^* \exp\{-2\pi i \mathbf{h}.\mathbf{u}(\mathbf{r})\} \exp\{2\pi i \mathbf{h}.\mathbf{u}(\mathbf{r} + t\mathbf{h}/|\mathbf{h}|)\} \\ &= FF^* \exp\{2\pi i \mathbf{h}.[\mathbf{u}(\mathbf{r} + t\mathbf{h}/|\mathbf{h}|) - \mathbf{u}(\mathbf{r})]\}. \qquad \ldots\ldots(7) \end{aligned}$$

The mean value of $F'F'^*$ cannot be evaluated exactly without assuming a particular variety of distortion. It is, however, highly improbable that a cold-worked metal would contain *periodic* distortions, and for non-periodic distortions the following plausible arguments lead to an approximate general evaluation. For large values of t the relative displacements of the cells will be large and random, so that the mean value of $F'F'^*$ will vanish. For small values of t, $\mathbf{u}(\mathbf{r} + t\mathbf{h}/|\mathbf{h}|)$ may be expanded in a power series in t, and terms in t^2 and beyond neglected. Then

$$\begin{aligned} J_t = \overline{F'F'^*} &= FF^* \overline{\exp\{2\pi i \mathbf{h}.[\mathbf{u}(\mathbf{r}) + (t/|\mathbf{h}|)\mathbf{h}.\nabla\mathbf{u} + \ldots - \mathbf{u}(\mathbf{r})]\}} \\ &\doteqdot FF^* \overline{\exp\{2\pi i t \mathbf{h}.\nabla\mathbf{u}.\mathbf{h}/|\mathbf{h}|\}}. \qquad \ldots\ldots(8) \end{aligned}$$

In this equation $\nabla\mathbf{u}$ is the tensor of which the strain tensor e_{ij} is the symmetrical part and the rotation tensor ω_{ij} is the anti-symmetrical part. It is readily verified that the tensile strain in the *hkl* direction, e_{hh}, is equal to $|\mathbf{h}|^{-2}\mathbf{h}.\nabla\mathbf{u}.\mathbf{h}$, so

$$J_t \doteqdot FF^* \overline{\exp(2\pi i |\mathbf{h}| e_{hh} t)}. \qquad \ldots\ldots(9)$$

Equation (9) should therefore be a good approximation to $\overline{F'F'^*}$ for any distribution of strains that makes J_t approach zero rapidly for large t. If the fraction of the crystal for which e_{hh} lies between e and $e + de$ is $\phi_{hkl}(e)de$, then

$$J_t = FF^* \int_{-\infty}^{+\infty} \phi_{hkl}(e) \exp\{2\pi i |\mathbf{h}| te\} de \qquad \ldots\ldots(10)$$

and

$$\begin{aligned} \epsilon &= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \phi_{hkl}(e) \exp\{2\pi i |\mathbf{h}| te\} de\, dt, \\ &= |\mathbf{h}|^{-1}\phi_{hkl}(0), \\ &= (\lambda/2\sin\theta)\phi_{hkl}(0), \qquad \ldots\ldots(11) \\ \beta &= \lambda/\epsilon\cos\theta = 2\tan\theta/\phi_{hkl}(0), \qquad \ldots\ldots(12) \\ \eta &= \beta\cot\theta = 2/\phi_{hkl}(0). \qquad \ldots\ldots(13) \end{aligned}$$

Measurements of integral breadths will therefore give $\phi_{hkl}(0)$. It is, however, possible to obtain $\phi_{hkl}(e)$ by a complete analysis of photometer curves of broadened and unbroadened lines. Suppose that the radiation reflected with an angular deviation between $2(\theta+\gamma)$ and $2(\theta+\gamma+d\gamma)$ is $I(\gamma)d\gamma$. Then, in the notation of this paper, equation (4) of Wilson (1943) may be written

$$I(\gamma)=N\int_{-\infty}^{+\infty} J_t \exp\{2\pi i M\gamma t\}dt, \qquad \ldots\ldots(14)$$

where N is the number of unit cells in the crystal and M is $2\cos\theta/\lambda$. On substituting the value of J_t from equation (10), this becomes

$$\begin{aligned} I(\gamma)&=NFF^*\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \phi_{hkl}(e)\exp\{2\pi i|\mathbf{h}|te\}\exp\{2\pi iM\gamma t\}dt \\ &=NFF^*\phi_{hkl}(-M\gamma/|\mathbf{h}|) \qquad \ldots\ldots(15)\end{aligned}$$

or

$$\frac{\phi_{hkl}(e)}{\phi_{hkl}(0)}=\frac{I(-|\mathbf{h}|e/M)}{I(0)}=\frac{I(-e\tan\theta)}{I(0)}. \qquad \ldots\ldots(16)$$

Thus ϕ_{hkl} is the same function of e as I is of $-e\tan\theta$. The elimination of incidental broadenings from the observed photometer curves to obtain $I(\gamma)$ involves Fourier analyses of both sharp and broadened lines. It is being treated elsewhere by one of us (Stokes, 1944).

§ 3. CALCULATION OF THE INTEGRAL BREADTHS FOR PARTICULAR MODELS

The problem of calculating β is thus reduced to the problem of calculating the fraction of the crystal for which the tensile strain in the *hkl* direction lies between 0 and de, i.e. $\phi_{hkl}(0)de$. This can be done if some particular model for the distortion is assumed, or by the use of approximations. Various approximations which suggest themselves lead to the result that $\beta\cot\theta$ is a function of $H=(k^2l^2+l^2h^2+h^2k^2)/(h^2+k^2+l^2)^2$, but the exact form of the function depends on the approximations. Two of the simplest are

(i) all values of $|e_{hh}|$ between zero and a maximum equally likely, and $e_{hh}=$ Direct Stress/Young's Modulus; or

(ii) mean value of $\exp\{ix\}$ equal to $\exp\{-\overline{x^2}/2\}$, where $\sqrt{\overline{x^2}}$ is the root mean square value of x, the stress being isotropic on the average in each case.

The assumption (ii) is exact if x is distributed according to a Gaussian error curve, and is in any case true as far as terms in x^3. One would expect, therefore, that (ii) would always be a fair approximation.

On approximation (i), $\phi(0)=1/2(e_{hh})_{\max}$, and

$$\eta=\beta\cot\theta=4(e_{hh})_{\max}. \qquad \ldots\ldots(17)$$

If the assumption that the maximum stress is independent of direction is made, the maximum value of e_{hh} will be the maximum stress $p_{\max}$ divided by the appropriate value of Young's Modulus, i.e.

$$\beta\cot\theta=4p_{\max}\{s_{12}+2s_{44}+(s_{11}-s_{12}-2s_{44})(h^4+k^4+l^4)/(h^2+k^2+l^2)^2\}. \qquad \ldots\ldots(18)$$

Except that it contains the maximum stress instead of the yield stress, this is the expression used by Stokes, Pascoe and Lipson (1943) in interpreting their results on copper filings. Since $h^4+k^4+l^4=(h^2+k^2+l^2)^2-2(k^2l^2+l^2h^2+h^2k^2)$, equation (18) may be written

$$\begin{aligned}\beta\cot\theta &= 4p_{\max}\{s_{11}-2(s_{11}-s_{12}-2s_{44})(k^2l^2+l^2h^2+h^2k^2)/(h^2+k^2+l^2)^2\}\\ &= A+BH,\end{aligned} \qquad \ldots\ldots(19)$$

where A and B are constants for a given specimen, and

$$H \equiv (k^2l^2+l^2h^2+h^2k^2)/(h^2+k^2+l^2)^2.$$

Values of H for the reflections commonly appearing on Debye-Scherrer photographs are given in the following table.

Values of $H=(k^2l^2+l^2h^2+h^2k^2)/(h^2+k^2+l^2)^2$

hkl	$h^2+k^2+l^2$	H	hkl	$h^2+k^2+l^2$	H
100	1	0·000	410*	17	0·055
110	2	0·250	322*	17	0·304
111	3	0·333	330*	18	0·250
200	4	0·000	411*	18	0·102
210	5	0·160	331	19	0·274
211	6	0·250	420	20	0·160
—	7	—	421	21	0·190
220	8	0·250	332	22	0·316
300*	9	0·000	—	23	—
221*	9	0·296	422	24	0·250
310	10	0·090	500*	25	0·000
311	11	0·157	430*	25	0·230
222	12	0·333	510*	26	0·037
320	13	0·213	431*	26	0·250
321	14	0·250	333*	27	0·333
—	15	—	511*	27	0·070
400	16	0·000			

* Overlapping reflections.

On approximation (ii), equation (9) gives

$$J_t = FF^*\exp\{-2\pi^2|\mathbf{h}|^2\,\overline{e^2_{hh}}\,t^2\}, \qquad \ldots\ldots(20)$$

and hence

$$\begin{aligned}\epsilon &= J_0^{-1}\int_{-\infty}^{+\infty} J_t\,dt = (2\pi|\mathbf{h}|^2\,\overline{e^2_{hh}})^{-\frac{1}{2}},\\ &= (\lambda/2\sin\theta)(2\pi\overline{e^2_{hh}})^{-\frac{1}{2}},\\ \beta &= \lambda/\epsilon\cos\theta = 2(2\pi\overline{e^2_{hh}})^{\frac{1}{2}}\tan\theta,\\ \eta &= \beta\cot\theta = 2(2\pi\overline{e^2_{hh}})^{\frac{1}{2}}.\end{aligned} \qquad \ldots\ldots(21)$$

The same result is of course obtained by assuming that e_{hh} is distributed according to a Gaussian error curve. Evaluating the constants in

$$\phi_{hkl}(e) = C\exp\{-\alpha e^2\}$$

in terms of $\overline{e^2_{hh}}$ gives

$$\phi_{hkl}(e) = (2\pi\overline{e^2_{hh}})^{-\frac{1}{2}}\exp\{-e^2/2\overline{e^2_{hh}}\},$$

so

$$\eta = 2/\phi_{hkl}(0) = 2(2\pi\overline{e^2_{hh}})^{\frac{1}{2}}. \qquad \ldots\ldots(21)$$

The calculation of $\overline{e_{hh}^2}$ calls for some consideration. In terms of the strains referred to the crystal axes,

$$e_{hh} = (h^2e_{11}+k^2e_{22}+l^2e_{33}+2kle_{23}+2lhe_{31}+2hke_{12})/(h^2+k^2+l^2),$$

or, in terms of the stresses referred to the crystal axes,

$$\begin{aligned} e_{hh} = [&h^2(s_{11}p_{11}+s_{12}p_{22}+s_{12}p_{33})+k^2(s_{12}p_{11}+s_{11}p_{22}+s_{12}p_{33}) \\ &+l^2(s_{12}p_{11}+s_{12}p_{22}+s_{11}p_{33})+4s_{44}klp_{23} \\ &+4s_{44}lhp_{31}+4s_{44}hkp_{12}]/(h^2+k^2+l^2). \end{aligned} \qquad \ldots\ldots(22)$$

In finding the mean value $\overline{e_{hh}^2}$ of e_{hh}^2, it is necessary to evaluate an expression containing mean values of products of pairs of the ps. It can be shown that, when the statistical distribution of stress is spherically symmetrical,

$$\overline{p_{11}^2} = \overline{p_{22}^2} = \overline{p_{33}^2}, \qquad \ldots\ldots(23)$$

$$\overline{p_{22}p_{33}} = \overline{p_{33}p_{11}} = \overline{p_{11}p_{22}}, \qquad \ldots\ldots(24)$$

$$\overline{p_{23}^2} = \overline{p_{31}^2} = \overline{p_{12}^2}, \qquad \ldots\ldots(25)$$

$$\overline{p_{11}^2} - \overline{p_{11}p_{22}} = 2\overline{p_{12}^2}, \qquad \ldots\ldots(26)$$

$$\overline{p_{11}p_{12}} = \overline{p_{22}p_{23}} = \overline{p_{33}p_{31}} = \overline{p_{11}p_{13}} = \overline{p_{22}p_{21}} = \overline{p_{33}p_{32}} = 0, \qquad \ldots\ldots(27)$$

$$\overline{p_{11}p_{23}} = \overline{p_{22}p_{31}} = \overline{p_{33}p_{12}} = 0, \qquad \ldots\ldots(28)$$

$$\overline{p_{31}p_{12}} = \overline{p_{12}p_{23}} = \overline{p_{23}p_{31}} = 0. \qquad \ldots\ldots(29)$$

Using these relations and equation (22) gives

$$\begin{aligned} \overline{e_{hh}^2} = \{&[(h^2s_{11}+k^2s_{12}+l^2s_{12})^2 + \text{cyclic permutations}]\overline{p_{11}^2} \\ &+2[(h^2s_{12}+k^2s_{11}+l^2s_{12})(h^2s_{12}+k^2s_{12}+l^2s_{11}) + \text{cyclic permutations}]\overline{p_{11}p_{22}} \\ &+16s_{44}^2(k^2l^2+l^2h^2+h^2k^2)\overline{p_{12}^2}\}/(h^2+k^2+l^2)^2, \end{aligned}$$

which becomes on reduction

$$\begin{aligned} \overline{e_{hh}^2} &= (s_{11}+2s_{12})^2\overline{p_{11}^2} - 4s_{12}(s_{12}+2s_{11})\overline{p_{12}^2} \\ &\quad - 4[(s_{11}-s_{12})^2-4s_{44}^2](k^2l^2+l^2h^2+h^2k^2)(h^2+k^2+l^2)^{-2}\overline{p_{12}^2}, \qquad \ldots\ldots(30) \\ &= A'+B'H, \qquad \ldots\ldots(31) \end{aligned}$$

where A' and B' are independent of the order of reflection and depend only on the elastic constants of the metal and the mean square stresses. Then

$$\eta = \beta\cot\theta = 2[2\pi(A'+B'H)]^{\frac{1}{2}} \qquad \ldots\ldots(32)$$

$$= (A+BH)^{\frac{1}{2}}, \qquad \ldots\ldots(33)$$

$$\eta^2 = A+BH, \qquad \ldots\ldots(34)$$

where A and B are constants for a given specimen and

$$H \equiv (k^2l^2+l^2h^2+h^2k^2)/(h^2+k^2+l^2)^2.$$

Experimental results obtained at this laboratory on metal filings and wire are in fair agreement with equations (19) and (34). The results are not sufficiently accurate to distinguish between them, but on the whole (34) seems preferable,

§4. CRITICISMS

Since the calculation given above depends on a number of approximations it will be well to reiterate them. They are as follows:

(*a*) The effect of the rotation of the cells has been neglected in finding $F'F'^*$.

(*b*) The distortion is assumed to be such that the mean value of $F'F'^*$ tends to zero as t increases, and that $\mathbf{u}(\mathbf{r}+t\mathbf{h}/|\mathbf{h}|)-\mathbf{u}(\mathbf{r})$ can be expanded without going beyond the term in t for values of t for which $F'F'^*$ is not negligible.

(*c*) (1) In the approximation (i), leading to equation (19), only the direct stresses are taken into account. This renders equation (19) somewhat less plausible than equation (34).

(2) In the approximation (ii), leading to equation (34), the distribution of stresses is assumed nearly normal. A different distribution of stresses would, however, only have the effect of changing the constant $2(2\pi)^{\frac{1}{2}}$ in equation (21), and would not, therefore, alter the form of equation (34).

(*d*) It is assumed that the stress distribution is statistically isotropic. This is open to two objections. First, it gives rise to geometrically incompatible strains in differently oriented crystals. The true distribution is more likely to be something between isotropic stress and isotropic strain, but the variation of η with H should still be of the same general kind. Secondly, it neglects the fact that the shear stress in some directions is probably relieved by the action of slip planes in the crystal.

It seems certain, therefore, that with sufficiently precise measurements of integral breadths, equations (19) and (34) will be found inexact. The manner in which they break down will perhaps indicate where the treatment is in greatest need of refinement.

§5. ACKNOWLEDGMENTS

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FURTHER INVESTIGATIONS OF THE MAGNETIC PROPERTIES OF NON-HOMOGENEOUS SYSTEMS

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ABSTRACT. The use of cylindrical pole surfaces shaped in accordance with recent theoretical work has made it possible to measure the magnetic susceptibility of a non-homogeneous specimen without reference to its distribution in the specimen carrier. The new method will be particularly useful in the examination of weakly magnetic crystals. So far, it has been used to investigate dilute amalgams of some pure metals with mercury. The results of these and other measurements are discussed ; it is interesting that all metals so far investigated exhibit paramagnetism when in dilute solution in mercury to an extent which is usually compatible with an increase in the number of free electrons in the amalgam.

§ 1. INTRODUCTION

The magnetic properties of mercury amalgams have not been studied to an appreciable extent until recent years, although their electrical conductivities have received fair attention. In the measurements hitherto available, Davies and Keeping (1929) investigated the magnetic properties of amalgams of gallium, gold, indium and tin, Bates and Tai (1936) those of bismuth, copper, chromium and manganese, while Bates and Ireland (1937) examined silver amalgams. Bates and Illsley (1937) and Bates and Baker (1940) also worked with amalgams of the ferromagnetic metals iron, nickel and cobalt. The present work is part of a planned attempt to obtain data for other, outstanding, elements; and, as conditions are difficult for carrying through any comprehensive plan at the present time, it is thought worth while to report progress recently made with the metals aluminium, cadmium and zinc, and to record certain new data for gold and silver amalgams.

Magnetic data are of little value unless they are based on measurements made under widely varied experimental conditions, e.g. with a wide range of concentration at one temperature, or with one concentration over a reasonable temperature interval, etc. In the present work, the first aspect is chosen. In earlier work, the Curie method and the Gouy method were both used in unmodified forms to measure susceptibilities, but experience has shown that both may be unreliable in the case of amalgams, owing to the formation of regions of different physical properties which are non-uniformly distributed throughout the bulk of the amalgam.

Bates, Baker and Meakin (1940) overcame this difficulty to a great extent by using a special modification of the Curie method. They enclosed the liquid amalgams in cylindrical tubes which were mounted so that they moved along magnetic lines of force running between special cylindrical pole pieces in such a way that the force exerted on each element of amalgam was practically independent of its position in the tube (cf. Bates, 1939). The work was a definite advance, but a thorough re-examination of the data at the beginning of the present work convinced us that considerable improvement might still be effected. Steps were therefore taken in this laboratory to determine by calculation and by experiment the best form of the pole surfaces for our purposes, and Davy (1942) obtained a general equation for their shape, and it was checked by experiment.

In the Curie method the force acting on each element of volume v and susceptibility k relative to vacuum is given by $F = kH\frac{dH}{dr}v$ or $\frac{k}{2}\left(\frac{dH^2}{dr}\right)v$. For this force to be independent of the position of the volume v inside a specimen tube, the quantity dH^2/dr must be constant throughout the tube. The use of vertical curved pole surfaces which are sufficiently deep means that the element may certainly occupy any position along a vertical direction in the tube without change in force upon it. Consequently, we have merely to satisfy ourselves that it may also be displaced in any horizontal direction within the tube without change in force. Davy showed that this condition is satisfied when each deep vertical pole face is of such a shape that it intersects a horizontal plane according to the equation $r^{3/2}\cos\frac{3}{2}\theta =$ constant, where r, θ are polar co-ordinates with reference to any previously fixed origin, and the constant is, of course, different for the two pole-faces.

Somekh (1943) has given a shortened proof of this requirement, and for this we may refer to figure 1, where the tube S, which contains the material under examination, is placed as nearly as possible in the plane of symmetry indicated by the dotted line in figure 1 (*a*). This line also represents the direction of the radius vector along which the magnetic force on the specimen is supposed to act, and along which dH^2/dr is constant, and on which the origin O is located. Assuming that the permeability of the pole-faces is infinite, i.e., that the profiles of the pole pieces in a horizontal plane are equipotentials, we want, firstly, $H\frac{dH}{dr}$ to be constant at any point (r, θ) in the horizontal plane, and this means that $H^2 = Ar$, where $H = 0$ when $r = 0$, and A is a constant. Hence,

$$H^2 = H_r^2 + H_\theta^2 = Ar, \qquad \ldots\ldots(1)$$

where H_r and H_θ are the components of the field parallel and perpendicular to the radius vector respectively. We want, secondly, the magnetic force to be directed along the radius vector, which means that

$$\frac{1}{r}\left(\frac{\partial H^2}{\partial\theta}\right)_r = 0,$$

or, that from the first condition,

$$H_r\left(\frac{\partial H_r}{\partial\theta}\right)_r = -H_\theta\left(\frac{\partial H_\theta}{\partial\theta}\right)_r. \qquad \ldots\ldots(2)$$

Let the equation for the potential V at the point (r, θ) be $V = Bf(r)F(\theta)$, where B is a constant. Then $H_r = -Bf'(r)F(\theta)$ and $H_\theta = \frac{-B}{r}f(r)F'(\theta)$, so that, on substituting in (2), we have

$$\left[\frac{rf'(r)}{f(r)}\right]^2 = -\left[\frac{F''(\theta)}{F(\theta)}\right] = K^2. \qquad \ldots\ldots(3)$$

Since the equation holds for all values of r and θ, K^2 is a constant. A solution of equation (3) is $V=Br^{\alpha}\cos\alpha\theta$, whence, on substituting in (2), we find $B^2\alpha^2r^{2(\alpha-1)}=Ar$, so that, by equating coefficients, $\alpha=\frac{3}{2}$, and, therefore, $V=Br^{3/2}\cos\frac{3}{2}\theta$. Finally, because V is constant, $r^{3/2}\cos\frac{3}{2}\theta=\mathit{constant}$ is the equation of a pole surface.

On this basis, the pole pieces P_1 and P_2 of figure 1 were cut. P_1 was 15 cm. wide and 7·5 cm. deep, with $r=11$ cm. for $\theta=0$, i.e. $OO_1=11$ cm., so that the equation for P_1 was $r^{3/2}\cos\frac{3}{2}\theta=11^{3/2}$. In the case of P_2, with $r=8$ cm. for $\theta=0$, i.e. $OO_2=8$ cm., the corresponding equation was $r^{3/2}\cos\frac{3}{2}\theta=8^{3/2}$.

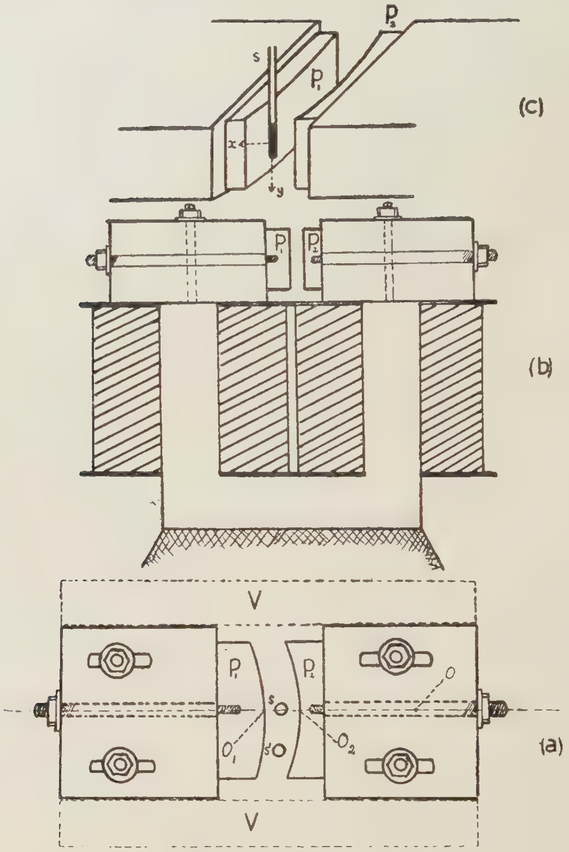

Figure 1. Arrangement of pole pieces and specimen tube.

The minimum separation of the pole surfaces along the line of centres was $OO_1-OO_2=11{\cdot}0-8{\cdot}0$ cm., the relative position of the pole pieces being thus fixed, once the shapes of the pole-faces are chosen. The importance of such pole faces to provide fields for the investigation of the directional magnetic properties of single crystals is obvious.

§ 2. EXPERIMENTAL PROCEDURE

The experimental arrangements followed closely those described by Bates, Baker and Meakin (1940), figure 2 of their paper being relevant. Pyrex glass tubes S and S^1 were suspended from an aluminium cross-bar, as shown therein and in figure 1 here, S being the specimen tube in which was placed the material under test and S^1 mainly a counterpoise. The tubes were evacuated by the special method described in their paper, and were hooked on a moderately robust copper frame (ff). The cross bar was adjusted to a standard horizontal position by using brass nuts (W and W^1) with the aid of a cross-wire image reflected from a mirror (M_2) mounted on the brass rod. The upper end of the latter was attached to an electrodynamometer coil (C), 2·5 cm. in mean diameter, consisting of about 50 turns of enamelled copper wire cemented together. This was suspended by a wire of B.O. 181 alloy to lie between the fixed coils (C_1 and $C_1{}^1$), each consisting of 800 turns of copper wire wound on ebonite formers; the mean diameter of each fixed coil was 9·0 cm., and their centres were 6·54 cm. apart. The torsion constant of the alloy was approximately 3·6 dyne cm. per radian. The specimen tube was surrounded by a water jacket V through which water, normally at 14° c., flowed at a constant rate.

When the magnetic field was excited, the tubes S and S^1 experienced forces, that on S being the greater, normally directed away from P_1, as both tube and pure mercury are diamagnetic. Consequently, a couple acted upon the suspended system and could be balanced by sending a suitable alternating current through the electrodynamometer coils to bring the moving system to a standard position, as shown by an image of a cross-wire reflected from a mirror (M_1) on to a scale (Sc) which was viewed through a telescope. The alternating current flowed through a 100-ma. vacuum thermo-junction joined to a Cambridge universal galvanometer whose pointer was viewed through a telemicroscope with a fine scale in the eyepiece, which allowed the position of the pointer to be found with great precision. The deflection was calibrated by sending a direct current through the thermo-junction, such that the pointer recorded the same deflection as that previously noted. The direct current was then measured by a potentiometer method.

Assuming that the specimen tube contained m_{Hg} gm. of pure mercury, the distance between the axes of S and S^1 was $2a$, the plane containing these axes made an angle ϕ with the direction of the field acting on S, and that the direct current for equilibrium in the standard position was i_{Hg}, then

$$\Gamma i_{\mathrm{Hg}}^2 + C\theta_1 = a\sin\phi m_{\mathrm{Hg}}\chi_{\mathrm{Hg}}H\frac{dH}{dr} + E, \qquad \ldots\ldots(4)$$

Γ being the electrodynamometer couple for 1 ampere, C the torsion constant of the suspension, θ_1 the torsion in the suspension and E the magnetic couple acting on the tubes when both were empty. In the latter case, in like manner,

$$\Gamma i_0{}^2 + C\theta_0 = E. \qquad \ldots\ldots(5)$$

Subtracting (5) from (4),

$$\Gamma(i_{\mathrm{Hg}}^2 - i_0{}^2) + C(\theta_1 - \theta_0) = a\sin\phi m_{\mathrm{Hg}}\chi_{\mathrm{Hg}}H\frac{dH}{dr}. \qquad \ldots\ldots(6)$$

Similarly, when S contained m_{A} gm. of amalgam,

$$\Gamma(i_{\mathrm{A}}{}^2 - i_0{}^2) + C(\theta_2 - \theta_0) = a\sin\phi m_{\mathrm{A}}\chi_{\mathrm{A}}H\frac{dH}{dr}, \qquad \ldots\ldots(7)$$

so that

$$\chi_{\mathrm{A}} = \frac{\Gamma(i_{\mathrm{A}}{}^2 - i_0{}^2) + C(\theta_2 - \theta_0)}{\Gamma(i_{\mathrm{Hg}}^2 - i_0{}^2) + C(\theta_1 - \theta_0)}\frac{m_{\mathrm{Hg}}}{m_{\mathrm{A}}}\chi_{\mathrm{Hg}}. \qquad \ldots\ldots(8)$$

The success of the method depended greatly upon the constancy of $H\frac{dH}{dr}$ for elements of volume occupying positions within S along the y direction of figure 1 (c) and for elements of volume within S when displaced along the x direction. The constancy in the y direction was examined both by a fluxmeter method and by using different quantities of pure mercury in S, since, for a chosen position of S, there should be a direct linear relation between the magnetic force and the mass of mercury. This was satisfied unless the mass of mercury exceeded 8 gm. The constancy in the x direction was tested by measuring the restoring couple when S was displaced through the comparatively large distance of 1·5 mm. from its normal position, the change in $\sin\phi$ being negligible as ϕ was very nearly 90°. The restoring couple was constant within less than 0·5 %.

In order to have positive quantities within the brackets of equation (8), Γi_0^2 was arranged to be of opposite sense to Γi_{Hg}^2 and Γi_{A}^2. The restoring couple per gm. of pure mercury was given by equation (4), and the apparatus was frequently calibrated by determining it at regular intervals. This was particularly convenient as the amalgams were made by adding quantities δm of a pure metal to a known mass m_{Hg} of mercury, which could also be used for the calibration, within the specimen tube. The mercury was heated to 80° c. *in vacuo* after preparation by the methods elaborated in earlier papers (Bates and Baker, 1938). After addition of metal, the tube was heated to an extent which depended on the metal, and the susceptibility was eventually found under conditions which were standardized as far as possible.

The concentration of the metal in the amalgam was $100\,\delta m/(\delta m + m_{\mathrm{Hg}})$ per cent, and the values of $(\chi_{\mathrm{A}}/\chi_{\mathrm{Hg}}) - 1$ for several metals at stated concentrations are reproduced in the accompanying graphs. Assuming the correctness of Wiedemann's law, the values of the apparent mass susceptibility χ_{M} of the metal in the amalgam were calculated and graphs of $\chi_{\mathrm{M}}/\chi_{\mathrm{Hg}}$ obtained.

It will be observed in the detailed record of results below that the difference between the susceptibility of an amalgam and the susceptibility of pure mercury never exceeded 5 % of the value of the latter. Consequently, even a tiny trace of ferromagnetic impurity would have serious effects. It is therefore essential to be able to detect the presence of such impurity by making measurements at different field strengths, etc. We made experiments with nickel amalgams, previously studied by Bates and Baker (1940), which are paramagnetic following their preparation by electrolysis, but become ferromagnetic on heating to 220° c. The susceptibility is then no longer independent of field strength. We found that the ferromagnetism was readily detected when measurements were made in three different fields, fixed by three chosen values of the electromagnet current, before and after heating; indeed, we found traces of ferromagnetism even before heating. We could not, however, attempt to correct for ferromagnetic impurity unless we had a wider range of field and electrodynamometer current.

As an additional check on the presence of ferromagnetic impurity, the susceptibilities of the metals used in the present investigation were found, and their values agreed with those generally accepted. Again, amalgams were sometimes examined in fields of different intensities and the susceptibility values were found independent of the field, which would not be expected if ferromagnetic impurity were present.

§ 3. RESULTS

Gold amalgams. Thin foil of high-purity gold supplied by Messrs. Johnson and Matthey was cut into very small pieces and washed successively with caustic soda, concentrated nitric acid and distilled water and then dried. They were added to the mercury, and, although amalgamation proceeded more quickly when heat was applied, the product was less reproducible. Consequently measurements were made (*a*) with amalgams prepared with minimum heating and (*b*) with amalgams heated to 140° c. to 150° c. in the evacuated specimen tube for one to two hours, these amalgams being investigated after standing for about twelve hours.

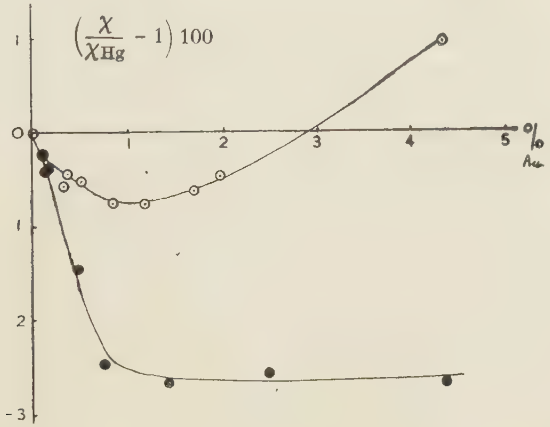

Figure 2. Gold amalgams.

Susceptibility of amalgam as a function of concentration.
● Freshly prepared ; ⊙ strongly heated and allowed to stand.

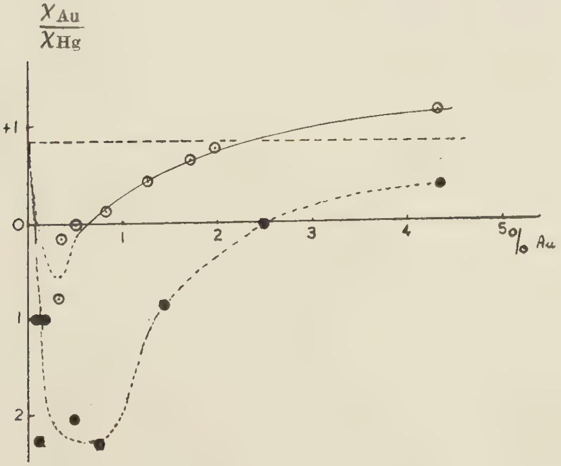

Figure 2 *a*. Cold amalgams.

Apparent susceptibility of gold as a function of concentration.
● Freshly prepared ; ⊙ strongly heated and allowed to stand.

The results are plotted in figures 2 and 2 *a*, the upper curve with encircled points being the curve for amalgams (*b*) which had been allowed to stand, the lower curve with encircled crosses being for freshly prepared amalgams (*a*); where χ_A is algebraically greater than $-0{\cdot}168\times10^{-6}$, the point lies below the axis of concentration. It is clear that in small concentrations gold dissolved in mercury is a paramagnetic, but the paramagnetism decreased with increase in concentration and also with additional heating and subsequent standing.

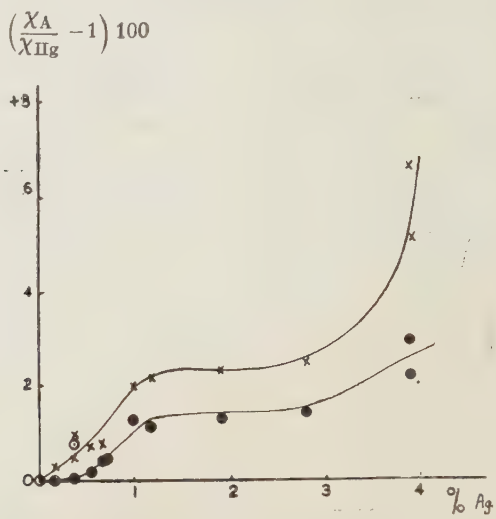

Figure 3. Silver amalgams.

Susceptibility of amalgam as a function of concentration.

● Freshly prepared, × after standing.

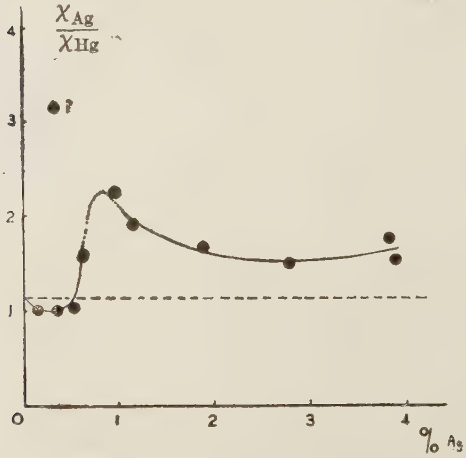

Figure 3 *a*. Silver amalgams.

Apparent susceptibility of silver as a function of concentration of freshly prepared amalgams.

The magnitude of the paramagnetism found at very low concentrations by Davies and Keeping was much greater than that recorded by us, but they do not state how they heated their amalgams, and, since they used gold in a powdered form, it is possible that small traces of paramagnetic impurities could have crept more easily into their specimens. The effect of standing is, of course, likely to facilitate the formation of molecular complexes of a diamagnetic character.

Silver amalgams. Very fine silver crystals were deposited on a loop of platinum wire by electrolysis of silver nitrate, using an anode of pure silver foil. The crystals were washed thoroughly with distilled water and dried. The silver amalgams were prepared like those of gold, but it was found that longer periods of heating were necessary to produce them. Susceptibility measurements were made immediately after preparation and also after standing for an interval of time sufficient to allow a stable state to be reached.

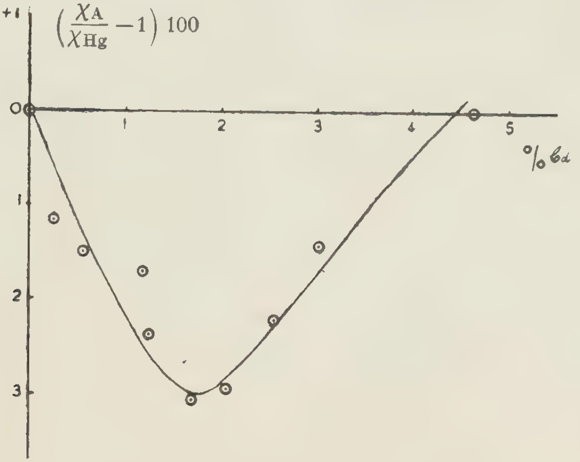

Figure 4. Cadmium amalgams.
Susceptibility of amalgam as a function of concentration.

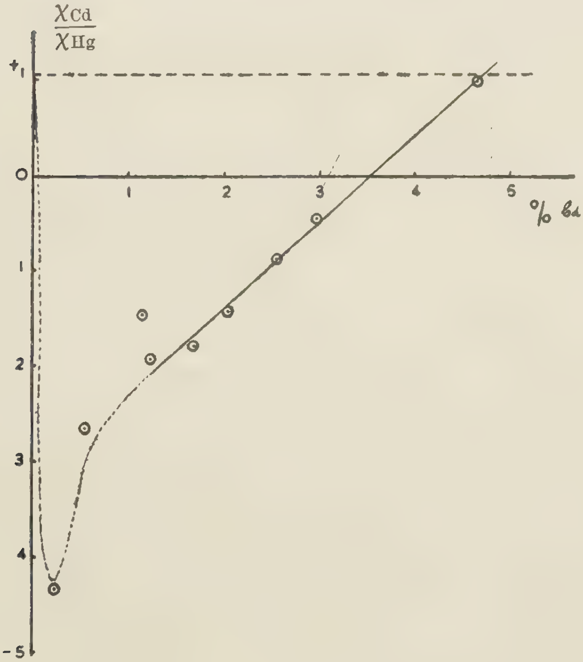

Figure 4*a.* Cadmium amalgams.
Apparent susceptibility of cadmium as a function of concentration.

The results are shown in figures 3 and 3 *a*, which show that silver dissolved in mercury as a weak diamagnetic. Initially, the addition of silver had little effect on the susceptibility of the specimen, but at about 0·5 % concentration the diamagnetism of the amalgam began to increase, although the measurements in this region were somewhat erratic, and, for this reason, a portion of the curve in figure 3 *a* is represented by a broken line. For small concentrations we obtained results in quantitative agreement with those of Bates and Ireland, but for large concentrations exact agreement was not obtained, as in these circumstances the Gouy method could not be as reliable as the present method.

Cadmium amalgams. Cadmium was scraped with a non-magnetic tool from Hilger rod of very high purity. Although it went readily into solution, trouble was encountered through the formation of an oxide film which was avoided only by evacuating the specimen tube before allowing the cadmium to reach the mercury. The results, in figures 4 and 4 *a*, show that cadmium behaved as a paramagnetic, especially when it was in minute concentration. While the paramagnetism decreased with increase in concentration, the magnetic properties of the amalgams did not change on standing, at any rate within the limits of experimental error.

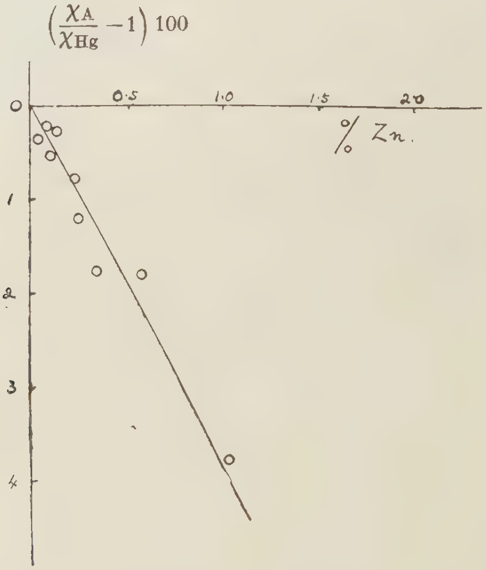

Figure 5. Zinc amalgams.
Susceptibility of amalgam as a function of concentration.

Aluminium amalgams. Attempts were made to prepare aluminium amalgams, but in the presence of mercury and atmospheric moisture the metal became coated with an oxide which prevented complete amalgamation, and we did not succeed in making satisfactory amalgams. It may be possible, later, to enclose a small quantity of aluminium sealed inside a very thin-walled glass tube and to break the tube inside an evacuated specimen tube containing mercury, but it will be a lengthy business.

Zinc amalgams. Small pieces of zinc were detached from a small rod of Hilger zinc by means of a non-magnetic tool, washed with a very weak solution of hydrochloric acid and dried with filter paper. Precautions similar to those with cadmium were adopted, except that the pieces of zinc were larger in order to avoid surface oxidation. The results, given in figure 5, show that zinc goes into solution as a paramagnetic. Since only low concentrations of zinc were used, a curve of χ_{M}/χ_{Hg} against concentration is not given, but from the tangent to figure 5 at the origin it was calculated that zinc possessed an atomic susceptibility of 67×10^{-6} e.m.u. per gm. atom under these conditions.

§ 4. DISCUSSION OF RESULTS

It is well known that the electrical conductivity of an amalgam is always greater than that of pure mercury, a feature which is readily explained if the dissolved metal exists in an ionized state. Now the importance of magnetic measurements on amalgams lies in the fact that they might give direct evidence concerning the ionic state of the dissolved metal, if attention were paid to the change in the number of free electrons brought about by solution. In the case of the more concentrated amalgams, the measurements might also give direct evidence of the formation of molecular complexes either with or without mercury atoms, since systems which possess an odd number of electrons ought to be paramagnetic because of the uncompensated spin of the odd electron, while systems with even numbers of electrons ought, generally speaking, to be diamagnetic.

For example, the normal state of an isolated copper, silver or gold atom is the $^2S_{1/2}$ state, and if it went into solution in mercury as a neutral atom it should cause a decrease in diamagnetic susceptibility corresponding to the gain of a magnetic carrier. If, however, the particle went into solution as a singly charged ion, the diamagnetic susceptibility should merely be increased by the addition of an atomic core. In like manner, the cadmium atom normally exists in a $^1S_0$ state, and would behave as a magnetic carrier if it went into solution as a singly charged ion. But this is not the whole story, for the electrons given up by the solute particle on ionization presumably remain in the amalgam to make a contribution to the free electron magnetism of the latter. The free or conduction electrons obey the Fermi-Dirac statistics, and on the application of a magnetic field may set either parallel or anti-parallel thereto. Since the energy is decreased when a spin sets parallel to the field, more electrons tend to set with parallel than with anti-parallel spin, and the former occupy higher quantum states, obtaining energy from the field in order to do so. Because the Fermi-Dirac distribution is so little affected by change in temperature, we thus get a type of temperature-independent paramagnetism. At the same time, these electrons exhibit a temperature-independent diamagnetism equal to one-third of the magnitude of their paramagnetism. Stoner (1935) showed that for ordinary temperatures the resultant gram-atomic susceptibility of free electrons is given by

$$(\chi_{A})_e \times 10^6 = \frac{32{\cdot}0}{V_0} q \left[1 - 6{\cdot}113 \times 10^{-9} \left(\frac{T}{V_0} \right)^2 \right],$$

where q is the number of free electrons per atom, and V_0 volts is the width of the energy band occupied by them, V_0 being of the order of a few volts. We may here neglect the term involving T^2, so that $(\chi_A)_e = \frac{32 \cdot 0}{V_0} q \times 10^{-6}$. We are interested here, of course, in the conduction electrons provided by solute particles.

The value assumed for the diamagnetism of an atomic core is very important, as may readily be appreciated by examining the case of silver in mercury. In very dilute solution the silver does not produce any measurable change in the magnetic susceptibility of the amalgam. Yet the value of the susceptibility given by Van Vleck (1932) and others for the core of the Ag^+ ion is -44×10^{-6} e.m.u. per gm. ion. Now the value for silver in dilute solution calculated from the present work and from that of Bates and Ireland is -18×10^{-6}. The difference, $+26 \times 10^{-6}$, must be attributed to the paramagnetism of free electrons or to paramagnetic ions. Let us assume that it is due entirely to free electrons, and that, in the above expression for $(\chi_A)_e$, $q = 1$; then the value of V_0 would be 1·23 volts, which, though low, is reasonable; but, clearly, the value obtained depends entirely upon the core correction.

The magnetic data now available are collected in the table (p. 193). For gold, the values obtained from Davies and Keeping's paper are given as well as our own; the discrepancy between them is undoubtedly due to differences in the methods of preparation and in experimental technique. The outstanding feature of the table is that, after allowance is made for the diamagnetism of the atomic core, every metal so far investigated enters into dilute solution in mercury as a paramagnetic. It is interesting to picture the ionic state in which each enters and to estimate the value of V_0 for the free electrons which are usually present.

It is clear that manganese occupies a special position in the table, because practically every particle must definitely exist as a magnetic carrier. If we assume that the carrier obeys Curie's law, we may obtain the effective magneton number, p_{eff}, of the ion by writing the expression $p_{\text{eff}}^2 \frac{5585^2}{3RT}$, equal to the corrected gm. ionic moment. In this way the value of p_{eff} is found to be 5·6. The agreement with the mean experimental value 5·85 (Bates, 1939, p. 130) is indeed striking, although it must be emphasized that the experimental evidence of the correctness of Curie's law, even in the case of ions in aqueous solution, is indeed meagre, and that the experiments of Bates and Tai (1937) showed manganese amalgams to possess a marked temperature hysteresis.

The high value of the gm. atomic moment of nickel given in the table proves that some of the nickel particles must exist as ionic carriers, presumably as Ni^+ in a ${}^4F_{9/2}$ state, or, more probably, as Ni^{++} in a ${}^3F_4$ state, for which the theoretical value of p_{eff}, given by $\sqrt{4S(S+1)}$, for the quenched state, is equal to 2·83.

The data for copper are interesting, because the low value of the gm. atomic moment means that the ion cannot exist in the form Cu^{++}, which, in the normal ${}^2D_{1/2}$ state, is a magnetic carrier. It must therefore exist as Cu^+, and the value (a) for the corrected gm. atomic moment is calculated on the basis of Pauling's (1927) value of -13×10^{-6} e.m.u. per gm. ion for Cu^+, and the value (*b*) from the value -19×10^{-6} given by Angus (1932). The value of V_0 calculated from (*a*) is about twice that calculated from (*b*), and as the lower value in this case is likely to be the more correct, we have evidence in favour of Angus's method of calculating the core correction. We obtain further support if we take Kido's (1932) value for the gm. molecular susceptibility of CuCl and subtract therefrom the value of the gm. ionic susceptibility of Cl$^-$ given by Angus, when we obtain 1·4 volts as the value for V_0.

The data for chromium show that it cannot exist in mercury as Cr$^+$ in a $^6S_{5/2}$ state, as this is a carrier, but we can certainly assume that it exists as Cr^{++} in the $^5D_0$ state for which the value of p_{eff}, given by $g\sqrt{J(J+1)}$ for the unquenched condition, is equal to zero, while the value of V_0, 2·1 volts, is very satisfactory. Zinc obviously exists mainly as Zn^{++} in a $^1S_0$ state, but the small value of V_0 indicates the presence of a few magnetic carriers, probably Zn$^+$ in a $^2S_{1/2}$ state. The value of V_0 for gallium likewise provides evidence that while most of the element exists as Ga^{+++} in a $^1S_0$ state, a few Ga^{++} ions in a $^2S_{1/2}$ state may be present. Similarly, cadmium is present mainly as Cd^{++} in a $^1S_0$ state, but a few Cd$^+$ ions in a $^2S_{1/2}$ state may exist. Again, the majority of indium particles must exist as In$^+$ ions in a $^1S_0$ state, but a few may occur as In^{++} ions in a $^2S_{1/2}$ state.

Magnetic data for elements in dilute solution in mercury

	Atomic susceptibility × 10^6				
Metal	Experimental value	Corrected for ionic core	q	V_0 (calculated)	Authors
Cr	23	30	2	2·1	1*
Mn	13,700	13,700	2	—	1
Ni	700	713	2	0·09	2
Cu	−7·3	(*a*) 6 (*b*) 11·7	1	5·3 2·7	1
Zn	67	78	2	0·82	4
Ga	133	143	3	0·67	3
Ag	−18	26	1	1·23	4, 5
Cd	35	72	2	0·89	4
In	218	250	3	0·38	3
Sn	−10	32	4 2	4·0 3·3	3
Au	194 83	237 126	3	0·40 0·76	3 4
Bi	133	170	3	0·56	1

* 1. Bates and Tai (1936);
2. Bates and Baker (1940);
3. Davies and Keeping (1929);
4. Bates and Somekh;
5. Bates and Ireland (1937).

In the case of the remaining elements in the table, the correction for the diamagnetism of the atomic core was obtained by taking the gm. molecular susceptibility of an anhydrous halide from Landolt-Börnstein (Roth-Scheel), *Physikalisch-Chemische Tabellen*, 5 Aufl., additional volume 3, part 3, p. 2191, and subtracting the appropriate correction for the halogen ion therefrom. The result is very satisfactory in the case of tin, where we may safely conclude that the element exists in the form Sn^{++} with V_0 equal to 3·3, or in the form Sn^{++++}

with V_0 equal to 4·0. Gold certainly appears to exist in the form Au^{+++}, although the value of V_0 is so low. Incidentally, the value calculated from our results appears preferable to that obtained from the work of Davies and Keeping. A few atoms in the neutral $^2S_{1/2}$ state would, of course, cause a low value to be obtained for V_0. A similar remark applies to bismuth, which normally exists in a $^4S_{1/2}$ state.

According to the modern electron theory of metals, V_0 is the measure in equivalent volts of the maximum energy of a free electron at absolute zero. But, if the electron is only partly free, then V_0 is more likely to be a measure of the difference between the maximum and the minimum energy of an electron in a band. The low values of V_0 in the table could therefore be explained on these lines.

§ 5. CONCLUSION

The interest attaching to the present work lies in the development of an effective method of dealing with the susceptibilities of non-homogeneous substances. We have studied amalgams, but it is clear that non-homogeneous solids, and, in particular, crystals, could be effectively examined by the method. The main features of the experimental results are that all elements so far tested go into dilute solution in mercury, partly at any rate, as paramagnetics, and that most of them exhibit a degree of paramagnetism which is compatible with the predicted increase in the number of free electrons in the amalgam.

§ 6. ACKNOWLEDGMENTS

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IS AN INTERPRETATION OF QUANTUM PHENOMENA BY HIDDEN PARAMETERS IMPOSSIBLE?

By H. PELZER

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In last year's Guthrie lecture,* Prof. Whittaker mentioned the example of a beam of plane-polarized light-quanta passed through a Nicol prism as not explicable in a *crypto-deterministic* manner (i.e. by hidden parameters). Nevertheless two examples of mechanisms will be given which, although admittedly rather artificial, are capable of performing this allegedly impossible task.

In the first model, we introduce the hidden parameter by the hypothesis that the Nicol prism possesses a microstructure which in our model is represented by an imaginary grating of equidistant lines (but not acting as a diffraction grating) in a plane normal to the optical axis, the lines being parallel to the plane of polarization of the Nicol prism. The plane-polarized photons are represented by thin needle-like rods normal to the incident beam and normal to the plane of polarization of the incident beam, the length of the rods being equal to the spacing of the lines in our imaginary grating, representing the Nicol.

We postulate that only those rods are passed through this first grating which, impinging on the grating, touch any one of its lines. Whether a rod touches or not depends on the relative positions of rod and grating, and it can easily be seen that the geometric probability for touching (i.e. passing) is $\cos\beta$, where β is the angle between the planes of polarization of the incident beam and of the Nicol prism. We then assume that behind the first grating there is a second parallel grating which oscillates against the first one in an irregular manner, so that of the rods passed through the first only a fraction, $\cos\beta$, will be passed through the second grating (which is supposed to pass only rods touching its lines, as the first grating does). But whilst we postulate that the first grating left unchanged the orientation of those rods which it had let pass, we postulate that the second grating, in addition to its selectivity, turns all the rods it has passed into a direction normal to its lines (i.e. a polarization as that of the Nicol prism). Finally, we postulate that both the first and the second grating turn those rods which (not touching their lines) they did not pass into a direction parallel to their lines.

It can immediately be seen how this mechanism differs from any mechanism taken into account by Whittaker. The model attributes the hidden parameter at least partly to the Nicol prism, whilst Prof. Whittaker seems to consider only hidden parameters completely inherent to the individual photons. As mentioned by Prof. Whittaker, J. v. Neumann has shown that with such restriction (as hidden parameters inherent to the photon) it is indeed impossible to interpret quantum phenomenon by hidden parameters, but to prove this completely with the example of the Nicol prism and the photon one has to consider (what Prof. Whittaker perhaps omitted for the sake of brevity) how the beam of photons emergent from the Nicol prism would behave if passed through subsequent Nicol prisms with planes of polarization tilted against one another.

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* *Proc. Phys. Soc.* **55**, 464 (1943).

Turning now to our second model, it must be admitted that it would be physically more satisfactory if the hidden parameters were completely inherent in the photons, at least in regard to their behaviour at the first Nicol prism on which they fall (i.e. whether the photon is passed or not), whilst the hidden parameter as regards the interaction with a second Nicol prism on which the photons might fall after passing the first is determined by an overriding influence, due to the first Nicol prism, which completely reshuffles the hidden parameters. The writer of these lines is indebted to Dr. A. E. W. Austen for pointing out to him that a model of this kind is also possible, and for giving the following example:—

A set of balls of equal material and mass but of different diameters, due to different temperatures, is shot through a sieve which passes only balls with a diameter below a certain limit. Behind this sieve the balls which have passed are heated for a part of their further path, which varies from hole to hole of the sieve, thus giving the balls a new distribution of temperature. Therefore the sieve is responsible for a new distribution of diameters among the balls.

A model of this type† may have a greater appeal than the first to the physicist, and might also be able to describe the behaviour of a polarized beam of photons passed through a Nicol prism with an arbitrary tilt β of the plane of polarization, at the same time accounting for the behaviour of the photons when passed through further Nicol prisms,

The author is indebted to Prof. v. Neumann for pointing out the importance of considering more than one analysing test (passing through more than one Nicol prism), and wishes to remark that he personally is of the opinion that the quantum phenomena are truly indeterminate, but that the proofs given by Whittaker and v. Neumann are incomplete, inasmuch as they do not consider a certain type of hidden parameters, which, whilst explaining the observed phenomena in a crypto-deterministic way, are not subject to the objection that they permit the separation of a quantum mechanical assembly (necessarily possessing dispersion) into pure classes, which, indeed, as v. Neumann has proved, would lead to contradiction with established laws of physics.

† [*Note added in proof.* A very simple and straightforward model of the second kind is obtained from the assumption that every photon of a plane-polarized beam has a hidden parameter $\phi (0<\phi<\pi/2)$ and that it will pass any Nicol prism whose plane of polarization is tilted against the plane of polarization of the beam by an angle less than ϕ, whilst it will not pass any Nicol tilted by an angle greater than ϕ. If we assume that the number of photons in the beam, of parameters between ϕ and $\phi+d\phi$, is given by $\sin 2\phi \, . \, d\phi$, then it follows that $\int_{\beta}^{\pi/2} \sin 2\phi \, . \, d\phi = \cos^2 \beta$ photons will pass a Nicol prism of tilt β in agreement with experience.

Now if we assume that each photon retains its parameter after passing a Nicol, we come into contradiction with experiment, e.g. if a vertically polarized beam passing through a Nicol tilted at 45° to the vertical and emerging with halved intensity and polarized at 45° were passed through a second Nicol of horizontal (or vertical) plane of polarization, and if the photons emerging from the first Nicol retained their old parameters, so that the emergent beam contained only photons of parameters $\phi>45^\circ$, then all of them would pass through the second Nicol in contradiction with experiment, which demands that the intensity should be halved again. This last consideration seems to be the essence of v. Neumann's abstract general mathematical proof that an explanation of quantum phenomena by hidden parameters is impossible. If, however, we assume that a Nicol prism completely reshuffles the hidden parameters, but in such a way that the new distribution function of the emergent beam is again $\sin 2\phi \, . \, d\phi$ (which can be performed by a crypto-deterministically operating mechanism), then we are in complete agreement with experiment again.]

NOTE ON A PROBLEM IN RADIAL FLOW

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Communicated 14 *February* 1944 *by J. H. Awbery*

ABSTRACT. The problem of conduction of heat in a circular cylinder with constant flow at the surface is solved by the Laplace transformation method. A previous solution by Macey is shown to be not exact, but a good approximation, and its region of usefulness is compared with that of the other types of solution. It is shown that Macey's idea can be extended to other boundary conditions, constant temperature, or radiation, the result being that with any of these boundary conditions, and constant initial temperature, corresponding times t_1 for a slab, and t for a cylinder, can be found, such that the temperature distribution in the slab at time t_1 is a good approximation to that in the cylinder at time t. Numerical values of t_1 as a function of t are given.

§ 1. INTRODUCTION

In two recent papers in this Journal, Macey (1942) and Awbery (1943) discuss the equation of conduction of heat* for radial flow,

$$\frac{\partial^2 v}{\partial r^2} + \frac{1}{r}\frac{\partial v}{\partial r} - \frac{1}{\kappa}\frac{\partial v}{\partial t} = 0, \quad 0 \leqslant r < a, \quad t > 0, \qquad \text{......(1)}$$

with $v = V$, a constant, when

$$t = 0, \quad 0 \leqslant r < a, \qquad \text{......(2)}$$

and with boundary conditions

$$K\frac{\partial v}{\partial r} = -Q, \text{ a constant, for } \quad r = a, \quad t > 0, \qquad \text{......(3)}$$

and v to remain finite as

$$r \to 0, \quad t > 0, \qquad \text{......(4)}$$

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* The notation of Carslaw's "Conduction of Heat" is used here (temperature v, conductivity K, diffusivity κ), since other problems in conduction of heat will be discussed. v and κ are Awbery's M and a respectively.

Both authors develop special methods for the problem. Awbery (1943) gives a formal solution of Fourier-Bessel type; while Macey (1942) obtains a solution suitable for smaller values of the time, by an interesting argument, which, however, is not strictly mathematically justifiable.

The object of this note is, firstly, to remark that the standard procedure of operational methods, or the equivalent Laplace transformation method, leads very simply to types of solution suitable for both large and small values of the time. This is the case, not only for the relatively simple problem considered here, but for problems involving slabs, coaxial cylinders, or concentric spheres, and with more general boundary conditions than those usually considered (cf. Jaeger (1942)). Further, it can be verified that the solutions obtained in this way satisfy the differential equations and initial and boundary conditions, so they may be regarded as rigorously established.

Secondly, these solutions will be compared with the approximate ones obtained by Macey's method, and the question of whether that method can be used with other boundary conditions will be considered.

§2. SOLUTION USING THE LAPLACE TRANSFORMATION

The Laplace transformation method and notation will be used here (the corresponding Heaviside operational expressions differ only by a factor p) We write

$$\bar{v} = \int_0^\infty e^{-pt} v \, dt$$

(where p is a number with a positive real part) for the Laplace transform of v; then, multiplying (1) and (3) by e^{-pt} and integrating with respect to t from 0 to ∞, we obtain the subsidiary equation for $\bar{v}$ (for a fuller account of the procedure see, e.g., Carslaw and Jaeger (1938)):

$$\frac{d^2\bar{v}}{dr^2} + \frac{1}{r}\frac{d\bar{v}}{dr} - \frac{p}{\kappa}\bar{v} = -\frac{V}{\kappa}, \quad 0 \leqslant r < a, \qquad \ldots\ldots(5)$$

to be solved with

$$\frac{d\bar{v}}{dr} = -\frac{Q}{Kp}, \quad r = a, \qquad \ldots\ldots(6)$$

and $\bar{v}$ finite as $r \to 0$. ......(7)

The solution of (5), (6) and (7) is

$$\bar{v} = \frac{V}{p} - \frac{Q\kappa^{1/2} I_0(r\sqrt{(p/\kappa)})}{Kp^{3/2} I_1(a\sqrt{(p/\kappa)})}. \qquad \ldots\ldots(8)$$

To obtain the solution of equations (1 to 4) of Fournier-Bessel type we apply the inversion theorem for the Laplace transformation (cf. Carslaw and Jaeger (1938)) to (8), which gives

$$v = V - \frac{Q\kappa^{1/2}}{2i\pi K} \int_{\gamma - i\infty}^{\gamma + i\infty} \frac{e^{\lambda t} I_0(r\sqrt{(\lambda/\kappa)})}{\lambda^{3/2} I_1(a\sqrt{(\lambda/\kappa)})} \, d\lambda, \qquad \ldots\ldots(9)$$

where $\gamma > 0$. The contour integral (9) is easily shown to equal $2\pi\iota$ times the sum of the residues at its poles. These are: a double pole at $\lambda = 0$ with residue

$$-\frac{2Q\kappa}{Ka}\left(t + \frac{r^2}{4\kappa} - \frac{a^2}{8\kappa}\right), \qquad \ldots\ldots(10)$$

and simple poles at $\lambda = -\kappa\alpha_s^2/a^2$, where $\pm\alpha_s$ are the roots of

$$J_1(\alpha) = 0. \qquad \ldots\ldots(11)$$

The residue at the pole $-\kappa\alpha_s^2/a^2$ is

$$\frac{2Qa}{K} e^{-\kappa\alpha_s^2 t/a^2} \frac{J_0(r\alpha_s/a)}{\alpha_s^2 J_0(\alpha_s)}. \qquad \ldots\ldots(12)$$

Using (10) and (12) in (9), we have finally

$$v = V - \frac{Qa}{K}\left\{\frac{2\kappa t}{a^2} + \frac{r^2}{2a^2} - \frac{1}{4} - 2\sum_{s=1}^{\infty} e^{-\kappa\alpha_s^2 t/a^2} \frac{J_0(r\alpha_s/a)}{\alpha_s^2 J_0(\alpha_s)}\right\}, \qquad \ldots\ldots(13)$$

where the summation in (13) is over the roots of (11). This is the result given by Awbery.

The series (13) is unpleasantly slowly convergent for small values of t, say $\kappa t/a^2 < 0{\cdot}02$. To find solutions which can be used in this region, following Goldstein (1932), we expand the expression (8) in ascending powers* of $p^{-1/2}$, using the asymptotic expansions of the Bessel functions if r/a is not small, With that restriction we obtain

$$v = \frac{V}{p} - \frac{Q}{K} e^{-p^{1/2}(a-r)/\kappa^{1/2}} \left\{\frac{a^{1/2}\kappa^{1/2}}{r^{1/2}p^{3/2}} + \frac{\kappa}{8p^2 r^{1/2} a^{1/2}}\left(3 + \frac{a}{r}\right)\right.$$
$$\left. + \frac{\kappa^{3/2}}{128 a^{3/2} r^{1/2} p^{5/2}}\left(33 + \frac{6a}{r} + \frac{9a^2}{r^2}\right) + \ldots\ldots \right\}. \qquad \ldots\ldots(14)$$

The successive terms of (14) are interpreted using the results of Hartree (1936):

$$\int_0^\infty e^{-pt}(4t)^{1/2n} \chi_n(\tfrac{1}{2}xt^{-1/2})\,dt = p^{-1/2n-1} e^{-x\sqrt{p}}, \qquad \ldots\ldots(15)$$

where †

$$\chi_n(w) = \int_w^\infty \chi_{n-1}(\xi)\,d\xi, \qquad \ldots\ldots(16)$$

and

$$\chi_0(w) = \operatorname{erfc} w = \frac{2}{\pi^{1/2}}\int_w^\infty e^{-\xi^2}\,d\xi, \qquad \ldots\ldots(17)$$

These functions are tabulated for $n = 1$ and 2 by Hartree (very briefly by Jeffreys) and a recurrence formula for higher values of n is given. Using (15) in (14), we obtain

$$v = V - (Q/K)\{2(\kappa at/r)^{1/2}\chi_1[(a-r)/2(\kappa t)^{1/2}]$$
$$+ \tfrac{1}{2}\kappa t a^{-1/2} r^{-3/2}(a+3r)\chi_2[(a-r)/2(\kappa t)^{1/2}]$$
$$+ \frac{1}{16}(\kappa t/a)^{3/2} r^{-5/2}(33r^2 + 6ar + 9a^2)\chi_3[a+r)/2(\kappa t)^{1/2}] + \ldots\ldots\}$$
$$\ldots\ldots(18)$$

---

* This is the extension to Bessel functions of the expansion in a series of exponentials used with hyperbolic functions. Terms in $\exp[-p^{\frac{1}{2}}(a+r)/\kappa^{\frac{1}{2}}]$, etc., will also arise in (14), but for small values of the time those shown are more important unless r/a is small. The solution in that case is discussed by Goldstein.

† This notation is that of Macey (1942). Jeffreys (1931), p. 113, uses Φn, and Hartree (1936) i^nerfc.

§ 3. COMPARISON WITH THE RESULTS FOR A SLAB, AND DISCUSSION OF MACEY'S ARGUMENT

The equations of the corresponding problem for linear flow are (v_1 is written for temperature and t_1 for time in this case to facilitate comparison with the results for the cylinder; r is again used for the space variable):

$$\frac{\partial^2 v_1}{\partial r^2} - \frac{1}{\kappa}\frac{\partial v_1}{\partial t_1} = 0, \quad 0<r<a, \qquad \text{......(19)}$$

with

$$\frac{\partial v_1}{\partial r} = 0, \quad r = 0, \quad t_1>0, \qquad \text{......(20)}$$

$$-K\frac{\partial v_1}{\partial r} = Q, \quad r = a, \quad t_1>0, \qquad \text{......(21)}$$

$$v_1 = V, \quad t_1 = 0, \quad 0<r<a. \qquad \text{......(22)}$$

Proceeding as before, we obtain the solutions

$$v_1 = V - \frac{Qa}{K}\left\{\frac{\kappa t_1}{a^2} + \frac{r^2}{2a^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-)^n}{n^2}e^{-\kappa n^2\pi^2 t_1/a^2}\cos\frac{n\pi r}{a}\right\} \qquad \text{......(23)}$$

and

$$v_1 = V - \frac{2Q(\kappa t_1)^{1/2}}{K}\{\chi_1[(a-r)/2(\kappa t_1)^{1/2}] + \chi_1[(a+r)/2(\kappa t_1)^{1/2}]$$
$$+\chi_1[(3a-r)/2(\kappa t_1)^{1/2}] + \ldots\ldots\} \qquad \text{......(24)}$$

If we compare the solution (24) for the slab with the corresponding result (18) for the cylinder, it appears that the former is valid for all times, and quite rapidly convergent up to times at which the exponentials in (23) have disappeared. On the other hand, (18) is useful only in the range $0<\kappa t/a^2<0{\cdot}01$, and for not too small values of r/a. For larger values of $\kappa t/a^2$, (13) must be used, and several terms of the series may be necessary. Thus numerical calculations for the rod are distinctly shorter than those for the cylinder.

Macey's method is virtually the following: he notices that if t and t_1 are so great that the exponential terms in (13) and (23) may be neglected,

$$v(r, t) = v_1\left(r, 2t - \frac{a^2}{12\kappa}\right), \quad 0<r<a. \qquad \text{......(25)}$$

He then asserts that a relation of this type holds for all times, i.e. that corresponding to t a time $t_1(t)$ can be found, such that the temperature distribution over the cylinder at t is identical with that over the rod at t_1, that is,

$$v(r, t) = v_1(r, t_1(t)), \quad 0<r<a. \qquad \text{......(26)}$$

Then the temperature of the cylinder at time t can be calculated by using the value t_1 in the formulae for the slab, e.g. in (24).

To determine t_1 in terms of t he used the relation

$$\int_0^a rv(r, t)dr = \int_0^a rv_1(r, t_1)dr, \qquad \text{.......(27)}$$

which, using (24), gives his fundamental relation, or, using (23), gives

$$\frac{2\kappa t}{a^2} = \frac{\kappa t_1}{a^2} + \frac{1}{12} - \frac{8}{\pi^4}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^4}e^{-\kappa t_1(2n+1)^2\pi^2 a^2}, \qquad \text{......(28)}$$

Alternatively the relation*

$$\int_0^a v(r,t)dr = \int_0^a v_1(r,t_1)dr \qquad \ldots\ldots(29)$$

might have been used, This leads to

$$\frac{\kappa t_1}{a^2} = \frac{2\kappa t}{a^2} - \frac{1}{12} - 2\sum_{s=1}^{\infty} \frac{e^{-\kappa\alpha_s^2 t/a^2}}{\alpha_s^3 J_0(\alpha_s)} \int_0^{\alpha_s} J_0(x)dx, \qquad \ldots\ldots(30)$$

where the α_s are the roots of (11).

The fact that the values of t_1 as a function of t obtained from (28) and (30) are not identical disproves (26); they are, however, extremely close, and the results found by using t_1 obtained in this way in (23) or (24) are found to agree very well with the accurate solutions for the cylinder problem.

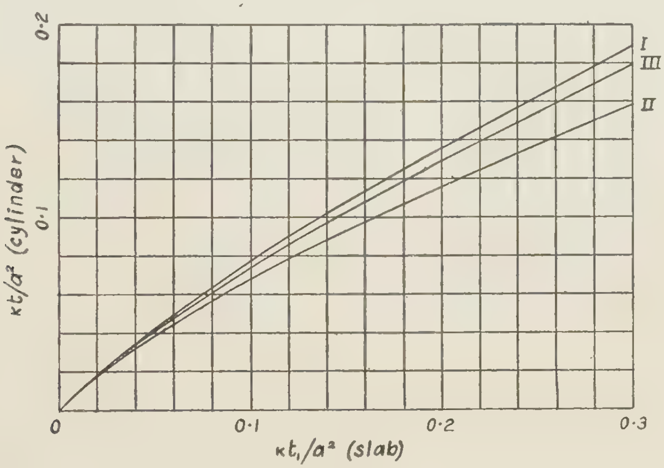

Figure 1. Corresponding times for slab and cylinder.

I. Constant flow, or radiation as $ah \to 0$.

II. Constant temperature, or radiation as $ah \to \infty$.

III. Radiation with $ah = 2$.

Thus it appears that the temperature distribution in a cylinder at time t with the boundary condition (3) and constant initial temperature is approximated sufficiently accurately for most physical purposes by the distribution in a slab with the same initial and boundary conditions at the "corresponding time" t_1 given by (28) or (30). In figure 1, curve I, t_1 as a function of t for this case is shown; the difference between (28) and (30) is too small to appear on this scale. For values of $\kappa t/a^2$ greater than those shown the result

$$\frac{\kappa t_1}{a^2} = \frac{2\kappa t}{a^2} - \frac{1}{12} \qquad \ldots\ldots(31)$$

may be used.

---

* (27) corresponds to using the solution for the slab in the cylinder, and comparing the average temperature thus obtained with that calculated directly. (29) corresponds to using the solution for the cylinder in the slab in the same way. Thus (27) and (29) have an equal physical status and the discrepancy between them should give an idea of the errors involved.

§ 4. EXTENSION TO OTHER BOUNDARY CONDITIONS

The question now arises whether this correspondence between the temperature distributions in a slab and a cylinder, with constant initial temperature, holds for other boundary conditions, such as constant surface temperature or radiation. Taking the case of constant surface temperature first, and with the same notation as before, we find, using (27),

$$\sum_{s=1}^{\infty} \frac{1}{\beta_s^2} e^{-\kappa\beta_s^2 t/a^2} = \frac{4}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\left\{1-\frac{2(-)^n}{(2n+1)}\right\} e^{-(2n+1)^2\pi^2 t_1/4a^2} \qquad \ldots\ldots(32)$$

or, using (29),

$$\sum_{s=1}^{\infty} \frac{1}{\beta_s^2 J_1(\beta_s)} e^{-\kappa\beta_s^2 t/a^2}\int_0^{\beta_s} J_0(x)dx = \frac{4}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2} e^{-\kappa(2n+1)^2\pi^2 t_1/4a^2}, \qquad \ldots\ldots(33)$$

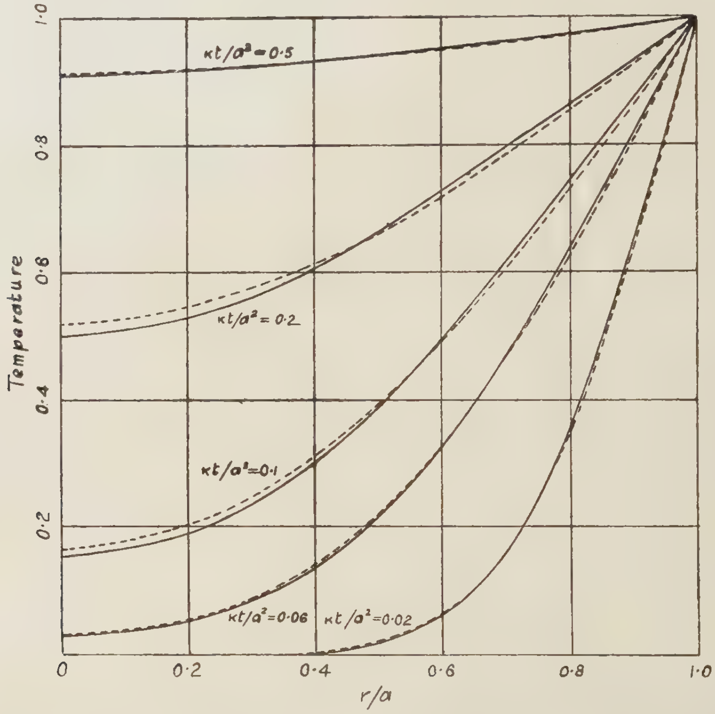

Figure 2. Comparison of accurate (full lines) and approximate (dotted lines) solutions for the temperature in a cylinder with zero initial temperature and unit surface temperature.

where $\pm\beta_s$ are the roots of

$$J_0(\beta) = 0. \qquad \ldots\ldots(34)$$

For large values of the time (32) and (33) give respectively

$$\kappa t/a^2 = 0{\cdot}4267(\kappa t_1/a^2) + 0{\cdot}0278 \qquad \ldots\ldots(35)$$

and

$$\kappa t/a^2 = 0{\cdot}4267(\kappa t_1/a^2) + 0{\cdot}0327, \qquad \ldots\ldots(36)$$

The difference between corresponding times determined from (27) and (29) is larger than in the previous case. Curve II in figure 1 is drawn as a mean of the two sets of values; for values of $\kappa t/a^2$ greater than those shown in figure 1 the mean of (35) and (36) may be used. The approximation is not so close as in the case of constant flux, but it is probably good enough for most physical purposes, as may be seen from the curves of figure 2, where the accurate values (full lines) and results obtained by using the corresponding times of figure 1 (dotted lines) are shown for various values of $\kappa t/a^2$, in the case of zero initial, and unit surface temperature.

If the boundary condition at $r=a$ is that of radiation, namely

$$\frac{\partial v}{\partial r}+hv=0, \qquad \ldots\ldots(37)$$

the same method may be used. From (27) we find

$$\sum_{s=1}^{\infty}\frac{ah}{(a^2h^2+x_s^2)x_s^2}e^{-\kappa x_s^2 t/a^2}=\sum_{s=1}^{\infty}\frac{(ah+1-\sec y_s)}{y_s^2(ah+a^2h^2+y_s^2)}e^{-\kappa y_s^2 t_1/a^2}, \qquad \ldots\ldots(38)$$

where the x_s are the roots of

$$xJ_1(x)=ahJ_0(x), \qquad \ldots\ldots(39)$$

and the y_s are the roots of

$$y\tan y=ah. \qquad \ldots\ldots(40)$$

For large t this gives

$$x_1^2(\kappa t/a^2)=y_1^2(\kappa t_1/a^2)+\ln\frac{ah(ah+a^2h^2+y_1^2)y_1^2}{(a^2h^2+x_1^2)(ah+1-\sec y_1)x_1^2}.$$

It is easy to show that in this case the curves of t against t_1 lie between those for constant flux and constant temperature, i.e. between curves I and II of figure 1. As $ah\to 0$ they approach curve I and as $ah\to\infty$ they approach curve II. The case $ah=2$ is shown in figure 1 as curve III.

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DISCUSSION ON BAND SPECTRA AND ENERGIES OF DISSOCIATION OF DIATOMIC MOLECULES

The discussion was based on the following papers :—

- R. F. Barrow and E. E. Vago, 1944 a. "An emission band system of PbSe". *Proc. Phys. Soc.* **56,** 76.
- R. F. Barrow and E. E. Vago, 1944 b. "The absorption spectrum of SnTe". *Ibid.* **56,** 78.
- A. G. Gaydon, 1944 a. "The band spectrum of NO: the gamma and epsilon systems". *Proc. Phys. Soc.* **56,** 95.
- A. G. Gaydon, 1944 b. "The band spectrum of N_2: weak systems in the visible region". *Ibid.* **56,** 85.

Dr. A. G. Gaydon, in opening the discussion, reviewed the methods by which the dissociation energies of diatomic molecules could be derived from data supplied by analyses of band spectra.

The Birge-Sponer extrapolation of vibrational energy levels to their dissociation limits was discussed, and the nature of predissociation and the use of such observations was dealt with, slides showing this effect in the spectra of CaH and MgH being shown. The form of the potential-energy curves for the various electronic states was discussed, and it was pointed out that in a few instances (CO, N_2, NO) the value for the dissociation energy obtained by use of predissociation observations indicated a violation of the non-crossing rule that the potential-energy curves for molecular states of the same electronic species must never cross. The possibility of maxima in the potential curves was stressed. For CO the observation of a weak, and rather doubtful, predissociation indicated a value for the dissociation energy of 9·14 ev., while the non-crossing rule required 11·11 ev. For N_2 a predissociation in the First Positive bands observed by van der Ziel (a slide of this was shown) appeared to require $D(N_2) = 7{\cdot}38$ ev., although no value below 8·5 could be reconciled with the non-crossing rule. (Since the discussion it has been shown (Gaydon, 1944 c) that van der Ziel's interpretation of the predissociation is not a unique solution, but that it would be consistent with a value for $D(N_2)$ of 9·764 ev., which now seems most probable.) Dr. Gaydon then went on to a brief discussion of his recent papers (1944 a and b, above, and 1944 d) on the spectra of NO and N_2, which favoured a higher value for $D(N_2)$ than 7·38 ev.

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Dr. R. F. Barrow. Although the spectroscopic properties of a limited number of diatomic molecules of special interest have been examined very thoroughly, much less is known about the variation of these properties in a group of chemically similar compounds. The hydrides, alkali metals, halogens and some groups of halides have been studied in varying degrees of detail (see, for example, Kronig, 1935; Pearse, 1939; Howell, 1943), but all these compounds represent a rather special valency type in which one of the constituent atoms can lose or gain only *one* electron in bond formation. The properties of the group of diatomic oxides, sulphides, selenides and tellurides of C, Si, Ge, Sn and Pb form an interesting study because of the possibilities of variations in the effective number of electrons involved in the bond in the different members of this series.

Early work showed the existence of ultra-violet electronic band-systems of CS and of SiO, probably analogous to the well-known $\mathrm{A}\,{}^1\Pi \rightleftharpoons \mathrm{X}\,{}^1\Sigma$ "Fourth Positive" system of CO; and systems of SnO, SnS and of PbO were familiar to the early spectroscopists (cf. Eder and Valenta, 1928). More recently, spectra of SiS, of the Ge compounds and of the series of selenides and tellurides have been obtained, some in emission in heavy-current positive-column discharge tubes and some in absorption. At the present time there are available some data from vibrational analyses for all the ground states and for one and, in a few cases, several excited states for nineteen of the twenty molecules of the group. We shall first discuss the constants derived from band-systems which appear to be related to the A $^1\Pi \rightleftharpoons$ X $^1\Sigma$ system of CO: the reasons for the selection of these particular upper levels, in cases where several such levels are known (i.e. Sn and Pb compounds), will be considered below.

Data from systems probably analogous to $A\,^1\Pi \rightleftharpoons X\,^1\Sigma$ systems of CO

The electronic energies relative to the ground state, ν_e, for the systems that are regarded tentatively as corresponding to the A $^1\Pi \rightleftharpoons$ X $^1\Sigma$ system of CO are plotted in figure 1 against *n*, the total number of extra-nuclear electrons. (There is no particular significance in the choice of this parameter, which is merely taken as a convenient function to give a rough numerical value to the complexity of the molecule.) The compound of highest electronic energy is CO: there is a sharp fall to SiO and thence a gradual shift in the direction of lower energies with increasing value of *n*. This behaviour recalls that shown by the

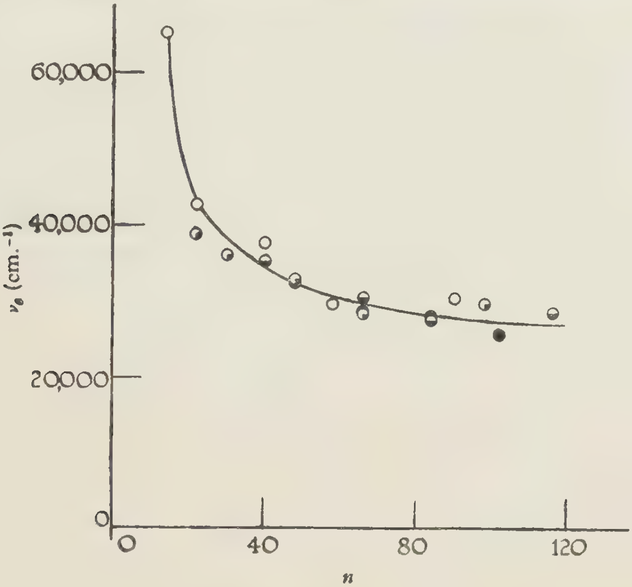

Figure 1. Electronic energy relative to ground state.

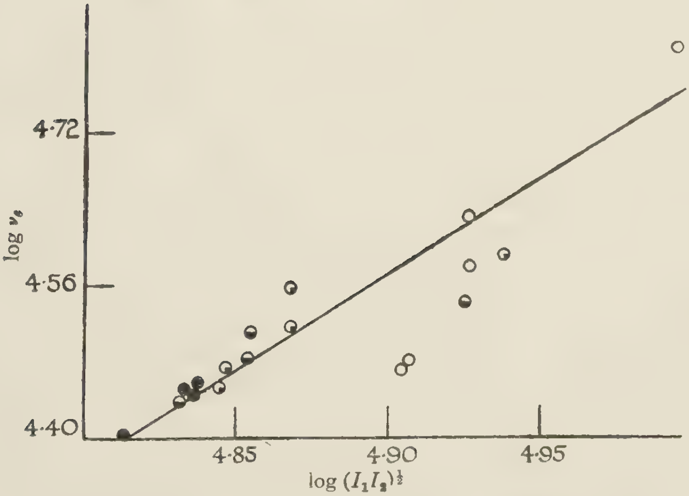

Figure 2. Electronic energy as a function of ionization potential.

ionization potentials of atoms in going down a vertical group in the periodic table: that there is a rough numerical parallelism is shown in the plot of log (ν_e) against log $(I_1 I_2)^{\frac{1}{2}}$, where I_1, I_2 are the ionization potentials of the constituent group -IV(b) and -VI(b) atoms (figure 2).

The vibration frequencies, ω_e, would be expected to decrease with increasing value of n on account of the purely physical relation of ω with the reduced mass, μ : $\omega = \frac{1}{2}\pi \sqrt{\kappa/\mu}$, but a variation in the product $\omega_e \mu^{\frac{1}{2}}$ would imply a variation in the force constant, κ. In fact it is clear from figure 3 that $\omega_e \mu^{\frac{1}{2}}$ suffers a considerable decrease with increasing n, particularly for the lighter molecules and in both excited and ground states.

The only values available for the energies of dissociation, D, for the states of these molecules, with the exception of CO, are those derived from the Birge-Sponer extrapolation, $D \sim \omega_e^2/4x_e\omega_e$. It is not possible to assess the probable errors of these values. For the ground state of CO the figure so derived happens to be in good agreement with what now appears on other grounds to be the most likely one (Gaydon, 1942); but there is considerable uncertainty, especially for the heavier molecules, in the values of $x_e\omega_e$ even for the ground states, while for the upper states the likelihood of unsuspected cubic terms in the vibrational energy function and the possibility of perturbations makes even a rough evaluation of D' impossible. However, the general trend of the variation of D'' with n (figure 4) does not appear to be in doubt: particularly notable is the very large decrease in D'' in going from CO (n=14) to $n \sim 50$, i.e. about 5ev.

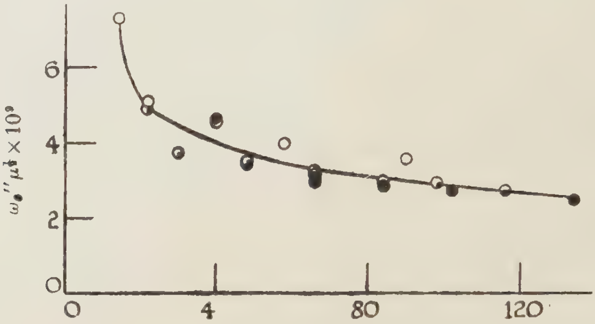

Figure 3 (*a*). Ground state vibration frequency.

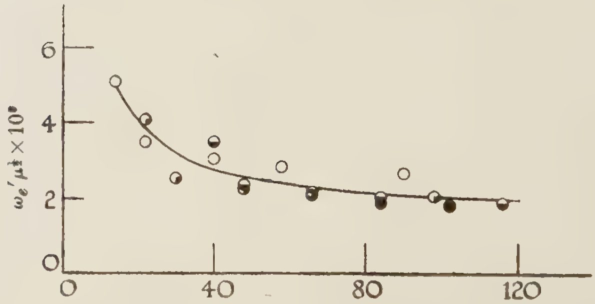

Figure 3 (*b*). Upper state vibration frequency.

This behaviour of the vibration frequencies and of the energies of dissociation suggests that, particularly towards the lighter end of the group, there are rather striking changes in the character of the valency bond between the two atoms. CO is, of course, a very singular molecule, in which a triple-bonded structure is believed to make a considerable contribution to the equilibrium state: it has, however, been suggested that such a contribution is considerably smaller in the case of CS (Pauling, 1940). In other words, the bond order appears to decrease in passing from CO to CS—and from the present data we might conclude that there is a further decrease in going from CS to PbTe.

Changes in the order of a bond have been closely identified with changes in bond lengths (e.g. Wrinch and Harker, 1940). Unfortunately, for only a few of the lighter molecules of this group have rotational analyses been done. The values at present known for the internuclear distances, r_e'', are given in table 1, where they are compared with the single-bond covalent distances calculated from the tables of Schomaker and Stevenson (1941). In all cases the latter are larger, but the trend of the differences is interesting. Thus for CO the observed bond length is about 0·3 A. smaller than the single-bond

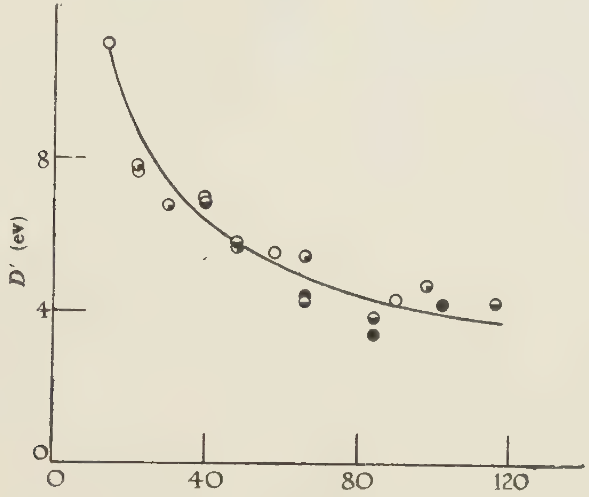

Figure 4. Energy of dissociation.

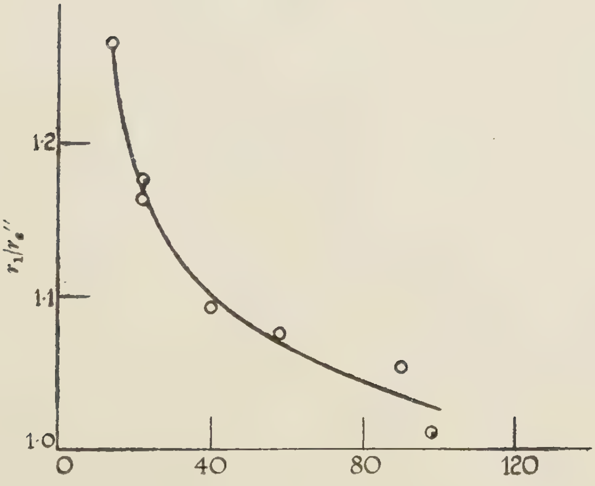

Figure 5. Internuclear distance.

covalent distance, in agreement with the contribution of 4- and 6-electron-bonded structures to this molecule, but for PbS the shortening is only 0·03 A., suggesting that here the link is largely uni-covalent. The ratio (uni-covalent distance)/r_e'' will be some direct function of the order of the bond. In figure 5 this quantity is plotted against n, and it will be seen that again the curve is of the same general shape as those shown in figures 1, 3 and 4. At one extreme is the highly individual molecule CO, with a bond order of something greater than two, and at the other end PbS, PbTe, in which the link seems to be a simple uni-covalent bond. Between these two we must conclude that there is a fairly smooth gradation of valency type.

Table 1. Values of r_e'' compared with the uni-covalent distances, r_1

Molecule	Number of electrons	r_e''* (A.)	r_1 (A.)	$(r_e''-r_1)$ (A.)
CO	14	1·128	1·42	−0·29
CS	22	1·536	1·81	−0·27
SiO	22	1·510	1·76	−0·25
GeO	40	1·651	1·80	−0·15
SnO	58	1·838	1·98	−0·14
PbO	90	1·923	2·04	−0·12
PbS	98	2·395	2·43	−0·03

* For references, see Herzberg (1939).

Excited levels of Sn and Pb compounds

In what has gone before it has been tacitly assumed that there is an unambiguous classification of excited states, such that these can be related back with some certainty to the $\text{A}^1\Pi$ state of CO. In fact, the correlation is fairly straightforward so long as we consider the emission spectra of the lighter molecules under certain experimental conditions. Thus for CS, CSe and the Si and Ge compounds only one ultra-violet system appears with any strength in emission in positive-column discharges. However,

Table 2. Spectroscopic constants of isoelectronic molecules *

Molecule	$\mu\times10^{24}$ (g.)	ν_e	ω_e (cm.$^{-1}$)	$x_e\omega_e$	Molecule	$\mu\times10^{24}$ (g.)	ν_e	ω_e (cm.$^{-1}$)	$x_e\omega_e$
(1) $n=22$									
SiO	16·80	42835	851·5	6·14	CS	14·40	38912	1072·3	10·3
		0	1242·0	6·05			0	1285·1	6·50
(2) $n=40$									
GeO	21·62	37762	651·3	4·24	CSe	17·19	35238	835·7	2·2
		0	985·7	4·30			? 0	1036·0	4·8
(3) $n=48$									
GeS	36·67	32890	375·0	1·51	SiSe	34·16	32449	403·4	3·2
		0	575·8	1·80			? 0	580·0	1·78
(4) $n=66$									
SnS	41·62	28338	331·9	1·25	GeSe	62·46	30432	272·4	1·05
		0	487·7	1·34			? 0	406·8	1·2
SiTe	37·92	28664	335·7	0·83					
		? 0	480·4	1·16					
(5) $n=84$									
SnSe	78·32	27549	226·4	0·86	GeTe	76·27	27970	219·4	1·3
		0	332·0	0·88			? 0	323·4	1·0

* For references, see Barrow and Jevons (1940) and Barrow and Vago (1943).

difficulties arise when we turn to the compounds of Sn and Pb, and when, in particular, we consider their absorption spectra. The known absorption spectrum of SnTe, for example, extends from about 2750 to 6500 A., and so far it has been analysed into five systems (Barrow and Vago, 1944) : there seems to be every possibility that extension of the experimental conditions will lead to the discovery of further systems.

Apart from purely experimental analogy, there is, however, one other observation which makes possible a fair guess at the upper level, which in some sense corresponds to the upper levels observed for the lighter molecules. This is the behaviour of isoelectronic pairs and groups (table 2). The similarity, which increases with increasing n, in the properties of these isoelectronic molecules is remarkable, and leads to a possible identification of the levels of SnS and of SnSe which are to be associated with the known "strong emission" levels of GeSe and SiTe and GeTe respectively. This identification has recently been confirmed, inasmuch as these selected levels of SnS and of SnSe have also been found to be those involved in the strong systems appearing in emission in positive-column discharges (Barrow and Vago, unpublished work and 1943).

Table 3. Spectroscopic data for Sn and Pb compounds

ν_e, ω_e, $x_e\omega_e$ (cm.$^{-1}$)

SnO	PbO	SnS	PbS	SnSe	PbSe	SnTe	PbTe
36803	35769	33037	—	(30700)	—	(27500)	(27200)
497·8	373·1	294·3	—	(205)	—	—	(135)
2·56	4·50	1·15	—	—	—	—	—
29625	30199	28338	29651	27549	28417	25444	—
582·6	530·5	331·9	299·3	226·4	190·5	179·1	—
3·08	2·92	1·25	1·57	0·86	0·6	0·40	—
—	—	—	(25024)	*	(23316)	21419	—
—	—	—	(284·0)	—	(183·0)	218·1	—
—	—	—	(1·17)	—	(0·25)	0·98	—
(25419)	(24864)	(23590)	(23213)	*	21006	20395	19763
(637·0)	(518·0)	(370)	(303·9)	—	184·8	239·3	145·5
(8·0)	(3·9)	—	(1·44)	—	0·43	1·53	0·46
—	22285	—	21848	(18900)	18717	16844	16362
—	498·0	—	282·2	(225)	166·9	178·5	141·4
—	2·20	—	0·86	—	0·14	0·44	0·22
—	19723	—	18851	(16815)	—	—	—
—	452·0	—	261·1	(225)	—	—	—
—	3·3	—	0·37	—	—	—	—
—	—	—	(14050)	—	—	—	—
—	—	—	(290)	—	—	—	—
—	—	—	—	—	—	—	—
0	0	0	0	0	0	0	0
822·4	721·8	487·7	428·1	332·0	277·4	259·5	211·8
3·73	3·70	1·34	1·20	0·88	0·56	0·50	0·12

Values in brackets are uncertain.

* Bands in the region 21500 to 23500 cm.$^{-1}$ have been measured by Walker, Straley and Smith (1938) and by Barrow and Vago (unpublished work).

The data at present available for the upper states of the Sn and Pb compounds are given in table 3, in which excited levels which are tentatively considered to be analogous are placed in the same horizontal rows. If this arrangement is correct, then it should clearly be possible to obtain new systems of many of these molecules involving excited states of lower ν_e than are at present known. The gaps and uncertainties in the table are as yet too numerous to make it worth while discussing this correlation in any detail but it may be noticed that the closeness of apparently analogous upper levels in the Sn and Pb compounds with a given non-metal is parallelled by the closeness of the ionization potentials of these two atoms, 7·30 and 7·38 ev. respectively.

These remarks have aimed at giving a rough qualitative picture of what appear to be the main variations of the spectroscopic properties of these molecules as we pass through the group. Much more experimental work is clearly required before any detailed interpretation can be attempted.

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Dr. R. C. Pankhurst. It is perhaps not always realized how uncertain the value of the energy of dissociation of the molecule may be when estimated by a method which involves extrapolation of the vibrational energy levels to their point of convergence, particularly when this point lies well above the highest level observed in the spectrum. Moreover, application of the Birge-Sponer equation

$$D = \omega_e^2/4x_e\omega_e$$

effectively makes use of only the lowest vibrational levels, since it neglects higher powers of v than the second in the expansion assumed for the energy $G(v)$. Again, this equation cannot be applied if, as in the excited states of the hydrides of the Group I (alkali) metals, the coefficient of u^2 in this expansion is positive ; for in such a case the vibrational energy interval initially increases, so that the lowest levels are actually diverging instead of converging.

As an example of the uncertainty which may occur in the estimated energies of dissociation, the values for sodium hydride may be cited. The value for the anomalous excited state may be deduced from that for the ground state together with the energy-difference between the ^2P and ^2S states of the sodium atom, into which hydride molecules in the excited and ground states respectively dissociate. Alternatively we may estimate the extrapolated contribution to the energy of dissociation using only the highest observed vibrational energies, for which the energy intervals decrease fairly regularly. The results thus obtained are 1·4 ev. and 2·1 ev., the large discrepancy representing uncertainties due, at least in part, to the considerable extrapolations involved : uncertainty of this type is liable to occur whenever the vibrational levels have not been observed to near their convergence.

Another feature in the representation of the behaviour of diatomic molecules which tends to be overlooked in the course of subsequent lengthy deductions is the arbitrary method of representing the potential energy as a function of internuclear distance. The principal criteria for any proposed potential function appear to be that it shall be physically plausible and that it shall lead to roughly the observed spacing of vibrational energy levels when used in the Schrödinger equation. Again, whatever potential function is adopted, it is important not to use it without reference to its inherent limitations: for example, Dunham's power-series expression, while designed to deal with rather greater distances from the equilibrium position than those covered by the simple parabolic expression, should not be applied without justification to very large internuclear distances, as any such power-series expression tends to $\pm\infty$ for sufficiently large values of the variable, whereas physical considerations require that the potential energy shall approach a finite limit corresponding to dissociation.

Dr. W. Jevons. Molecules composed of two group V atoms are of interest to the present discussion, as they have the same numbers of electrons, and are of nearly the same masses, as the molecules composed of a group IV and a group VI atom, discussed by Dr. Barrow, and the simplest of them, N_2, is the subject of one of the investigations described by Dr. Gaydon. Some spectroscopic resemblance between the two groups of molecules is to be expected, and does, in fact, exist.

Data for group V–V molecules are far less complete than for group IV–VI, even though each compound molecule of the former is comparable in mass and electron content with two molecules of the latter, e.g., PN with SiO and CS. Band-systems have been recorded for the five elementary molecules N_2, P_2, As_2, Sb_2, Bi_2, and for five of the compound molecules, namely, PN, AsN, SbN, BiN, SbBi. In every case, except that of BiN, for which no particulars seem to be available, the analysis has yielded data for the ground state, which is probably $^1\Sigma$ as in the case of each group IV–VI molecule.

Table 1. Values of ω_e and (in small type) of $x_e\omega_e$ for ground states ($^1\Sigma$)

(*a*) Group IV–VI

	${}_{8}$O	${}_{16}$S	${}_{34}$Se	${}_{52}$Te
${}_{6}$C	2168·2 13·04	1285·1 6·50	1036·0 4·8	
${}_{14}$Si	1242·0 6·05	749·5 2·56	580·0 1·78	480·4 1·16
${}_{32}$Ge	985·7 4·30	575·8 1·80	406·8 1·2	323·4 1·0
${}_{50}$Sn	822·4 3·73	487·7 1·34	332·0 0·88	259·5 0·50
${}_{82}$Pb	721·8 3·70	428·1 1·20	277·4 0·56	211·8 0·12

(*b*) Group V–V

	${}_{7}$N	${}_{15}$P	${}_{33}$As	${}_{51}$Sb	${}_{83}$Bi
${}_{7}$N	2359·6 14·44	1337·2 6·98	1068·0 5·36	942 5·6	
${}_{15}$P	1337·2 6·98	780·4 2·81			
${}_{33}$As	1068·0 5·36		429·4 1·12		
${}_{51}$Sb	942 5·6			272·8 0·62	
${}_{83}$Bi				220·0 0·50	173·7 0·41

For the known ground states, to which it is safest to confine discussion in the first instance, the vibrational coefficients ω_e and $x_e\omega_e$ are given in table 1 (*b*), those of group IV–VI molecules being set out in the same manner for direct comparison in table 1(*a*). The data for each compound molecule of group V–V appear twice in 1 (*b*), and those for a pair of isoelectronic (and almost equally heavy) molecules appear in corresponding places in 1(*a*) and 1(*b*), e.g. CSe and AsN in the top rows, and GeO and AsN in the left-hand columns.

The parallelism between the two groups is two-fold: not only are the trends of the coefficients similar, but the values of each of the vibrational coefficients are of the same order for any isoelectronic pair of molecules. It is evident that Dr. Barrow's treatment of these coefficients and the derived estimates of the energies of dissociation in group IV–VI could be applied to group V–V with roughly the same results

Special caution is necessary in seeking a similar parallelism between the coefficients for the known excited electronic states in the two groups, since the excited states of $P_2(^1\Sigma)$, $As_2(?\,^1\Sigma)$, Sb_2, $SbSi(?\,^1\,)$ and Bi_2 do not appear to be analogous to those of $N_2(a\,^1\Pi)$, $PN(^1\Pi)$, $AsN(?\,^1\Pi)$ and $SbN(?\,^1\Pi)$, and the data for excited states are even more fragmentary than for the ground states. All that can be asserted at present is that, corresponding to the well-known similarity between the upper states of the Fourth Positive system of $CO(A\,^1\Pi \rightleftharpoons X\,^1\Sigma)$ Lyman's system of $N_2(a\,^1\Pi \rightleftharpoons X\,^1\Sigma)$ there are striking numerical similarities between two of the three 22-electron molecules and between two of the three 40-electron molecules. This is evident from table 2, the figures for PN and AsN being much closer to those for CS and CSe, respectively, than to those for SiO and GeO, respectively. Between the available data for the 58-electron molecules comparison is hardly possible, as no band system has been recorded for CTe, and it is by no means evident which excited state of SnO should be chosen for comparison with that of SbN; in table 2 the data from the further ultra-violet system of SnO are used instead of those for the better-known visible system.

Table 2. Values of electronic energies and vibrational coefficients for excited states

Electrons	Molecule	ν_e	ω_e	$x_e\omega_e$
14	N_2 $(a\,^1\Pi)$	69623·1	1692·3	13·32
	CO $(A\,^1\Pi)$	65075·2	1515·6	17·25
22	PN $(^1\Pi)$	39805·6	1103·1	7·22
	CS $(^1\Pi)$	38912·1	1072·3	10·3
	SiO $(^1\Pi)$	42835·3	851·5	6·14
40	AsN$(?\,^1\Pi)$	36009·1	863·0	8·24
	CSe $(?\,^1\Pi)$	35238·0	835·7	2·2
	GeO$(^1\Sigma)$	37762·4	651·3	4·24
58	SbN$(?\,^1\Pi)$	34465	830·7	6·0
	CTe	?	?	?
	SnO	36803	497·8	2·56

A systematic investigation of group V–V is obviously desirable, and would in normal circumstances have been undertaken long before now.

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OBITUARY NOTICES

GEORGE LEONARD ADDENBROOKE

G. L. Addenbrooke, who died on 12 October 1943, entered the scientific profession, like many of his contemporaries, as a result of mature choice and not by way of a formal scientific education. The choice was not unexpected, seeing that he came from a family of ironmasters ; his father was a member of the first Council of the Iron and Steel Institute, while an ancestor founded Addenbrooke Hospital in the 17th century. Mr. Addenbrooke was born at Wombourn, near Wolverhampton, on 19 May 1860, was educated at Winchester, and followed a mercantile career for some years. He then made the decision which determined his future career and joined the engineering staff of the United Telephone Company in 1883, where he was associated in the first telephone cable trunk route with Ferranti, whom he accompanied to the Grosvenor Gallery Central Station, the first electric power station of its kind in the country. It was at this stage that his abiding interest in dielectrics arose, because both telephone and power cables were then insulated in a very crude manner. He used to recall that Professor Hughes insulated his apparatus by placing it on a table covered with sheets of newspaper, and quoted with amusement what he called the flounderings of the experts of the day in the enquiries and law cases over the failures of early telephone cables. Thereafter he pursued concurrently his engineering and his scientific interests. As an engineer he specialized in the development of public supply, and was associated with the first high-voltage overhead power lines in this country. In 1909 he gave three Cantor lectures on Electric Power Supply, the substance of which was published in three papers by the Institution of Electrical Engineers. In 1917 he was among those reporting on the Severn Barrage Scheme, and later on the co-ordination of Electric Supply. The former report led to the Government enquiry on the project, while the latter was a precursor of the action which led to the formation of the Electricity Commission and Central Electricity Board. Like many of his day, he carried on his scientific work in his private laboratory. In his last house at Holland Villas Road, Kensington, he set aside two large basement rooms as a laboratory and workshop in the old-fashioned style. His first work was on the measurement of alternating voltages, currents and power by means of electrostatic instruments of the quadrant-electrometer type. His papers on this subject were published in 1900 to 1903, and he made some beautiful instruments, which were still set up and in working order at the time of his death. With these instruments, based on the theories of Maxwell, to whom his notes made copious references, he was among the first to measure the energy losses in dielectrics and to show the existence of phenomena quite other than " insulation leakage ". He was among the first, if not the first, in this country to show the profound effect of moisture on dielectrics, including those, such as celluloid, hitherto thought to be unaffected ; here he had the gratification of having his findings confirmed by the failure of celluloid to protect certain exhibits at the South Kensington Museums. His own laboratory was something of a museum, for he preserved everything in working order, and some of his equipment had a working life of 30 to 40 years. This may have been due to the fact that Mr. Addenbrooke was an engineer—string and sealing wax had not their accustomed place in his laboratory. Consistently with this, his experiments were less discursive and more directed than was common in the private laboratories of physicists of that time. Few auxiliary experiments or the vestiges from incomplete schemes were to be found in his workrooms, although many still-born ideas are in his memoranda. He was more interested in results than methods ; apparatus was plant set up to yield a service, the acquisition of a series of results, and, once set up, it remained there as a permanent asset. He was a dexterous experimenter, and although handicapped by inability fully to comprehend the idiom of modern mathematical physics, his insight was uncommonly accurate. The problems he tackled were part of a field which remains still very imperfectly explored, and some of his more detailed ideas are yet valid. For example, he made a machine (still extant) for producing alternating currents of very low frequencies, and the significance of this range has been appreciated in relatively recent times. With advancing years his scientific interest remained unabated, and from 1920 he concerned himself with the meaning of the dielectric constant, or " dielectric attraction ", and its relation with other physical properties of the elements, resulting in a series of papers in the *Proc. Physical Society* and the *Philosophical Magazine.* Here again he perceived basic relations, although the quantitative theory was outside his particular scope. At his suggestion, and with his co-operation, measurements were made on bromine and carbon by his friends. The latter element was in the form of a very large number of diamonds which could only be borrowed for a short time, so that experiments had to continue night and day. Although over 70, Mr. Addenbrooke was present at several of the night watches. His belief in the importance of dielectric studies finds expression in his arrangement that a gift should be offered to the Physical Society to encourage scientific work of this nature at the Council's discretion, if possible as a prize awarded biennially. He numbered among his friends most of the leading figures in electrical science of his day, particularly Ferranti and Hughes, while only recently two of his contemporaries and friends predeceased him, Mr. Rollo Appleyard and Mr. Robert Paul. His personal address exemplified the motto of his school, and all who met him, young or old, were charmed with his courtesy and generosity. He will be held in affectionate remembrance by all those privileged to know him. He was a Fellow of the Physical Society (1925), Member of the Institution of Electrical Engineers (Associate 1884, Member 1891), member of the Council of the Royal Photographic Society (1887–1893), and a member of the Athenaeum and (formerly) of the St. Stephen's Clubs. He leaves a widow, an only daughter, Mrs. Marston, wife of Lt.-Colonel Marston, D.S.O., of Chalfont St. Giles, Bucks, and three grandchildren. S. WHITEHEAD.

ROBERT MORRISON ABRAHAM

Robert Morrison Abraham was the second son of William Abraham and Ann Morrison. He was born at Coleraine, Co. Londonderry, on 8 March 1879, and educated at the City and Guilds Technical College at Finsbury and at King's College, London. He later served an apprenticeship with the engineering firms of Coombe, Barbour and Coombe of Belfast and Siemens of Woolwich.

During the South African War he enlisted in Marshall's Horse, served through the war and received the Queen's Medal and Clasp. After peace was declared he was appointed Assistant Manager to the Cape Town Tramways Co., and subsequently Signalling Engineer to the Cape Government Railway. A few years later he resigned this post and proceeded to tour the world, eventually finding a suitable position with the American Automatic Signalling Co. Inc., of Buffalo, N.Y. It was the knowledge here acquired that stood him in such good stead when he returned to this country as Assistant-Manager of the British Pneumatic Railway Signal Company, Ltd. Whilst with this company he was given the job of designing and installing the signalling systems at Immingham Docks, Wath, Clapham Junction and Manchester. In later years he used to tell how he switched over all the signals at Clapham Junction from manual to automatic one midnight, and then sat tensely until seven in the morning, hoping the interlocking would not fail, breathing a sigh of relief when everything worked out smoothly as arranged.

His life-work really began in 1911, when he acquired an interest in C. F. Casella and Co., Ltd., an old-established firm of scientific instrument makers ; later he became also Managing Director of D. Gilson and Co., a firm making small parts for the electrical industry—a connection which was severed in 1928.

Abraham had a flair for designing efficient instruments, a good mathematical brain and great mechanical aptitude. He was particularly interested in meteorological instruments, and designed a recording rain-gauge which is in wide use. A standard barometer, fitted with an ingenious form of zero adjustment of his design, has proved very successful in practice. A manometer fitted with a somewhat similar zero adjustment is in use for determining differences of pressure as small as 0·01 inch of water. It has been found particularly useful for levelling large surfaces, such as printing-press beds, the jetty at the Ford works at Dagenham, etc.

He was one of the pioneers in this country in introducing divided glass circles into geodetic instruments. A patent (No. 274,185 of 1926) protected the design of a sextant with such a circle, with which it is possible to read directly to six seconds and to estimate to one second without difficulty. His internal focusing mechanism (Patent No. 9690, 1913) as applied to theodolite telescopes is in general use.

In later years he interested himself in astronomical instruments, and was largely responsible for the design of the micro-photometers and solar spectrographs supplied to the Oxford and Radcliffe (Pretoria) Observatories.

He was a prominent member of the Athenaeum, where he had a large circle of friends. His hobby in late life was making violins, and to this he brought the scientific knowledge of acoustics, the great mechanical skill he possessed and his love of music. The violins he made with his own hands were samples of perfect workmanship, and were used and praised by several leaders of orchestras in London. After his death, a memorial concert was given in which all the string instruments used, violins, viola and 'cello, were made by him. It was a great success and a fitting memorial to one side of his activities.

A complete account of violin construction, with scale drawings, written by him, was published in *The Strad* during 1942–43 ; this will be published in due course in book form after the war.

His other works were *Surveying Instruments* and two popular books, *Winter Nights Entertainments* and *Diversions and Pastimes*. In these latter he gathered together a series of mathematical and mechanical puzzles, described the technique of rope-splicing and gave descriptions of string figures. He illustrated both books with his own pen-and-ink sketches, for he was a good black-and-white artist. They were published simultaneously in London and New York and went through several editions.

Abraham was a Member of the Institution of Electrical Engineers and a Fellow of the Royal Astronomical Society. He was elected a Fellow of the Physical Society in 1911.

He died on 26 July 1943 at his home at Tewin, Herts. He is survived by his widow and three sons.

J. J. A.

HUGH FRANK NEWALL

PROF. H. F. NEWALL, F.R.S., who died on 22 February 1944, was the youngest son of Robert Stirling Newall, F.R.S., and was born on 21 June 1857, his mother being a daughter of Hugh Lee Pattinson, F.R.S. Thus there was scientific ability on both sides of his ancestry. His father, R. S. Newall, was the head of a firm of engineers at Gateshead-on-Tyne, specializing in the manufacture of submarine cables and wire ropes ; he was also keenly interested in astronomy. In 1863, on his order, Messrs. Cooke and Sons, of York, made a refracting telescope with an object glass 25 inches in diameter, the largest then known, the glass being obtained from Messrs. Chance, of Birmingham. Thus Hugh Frank grew up in a mental atmosphere of observational astronomy.

He went to school at Rugby, and thence to Trinity College, Cambridge, where he took his degree in 1880 in mathematics and natural sciences.

In 1881 he married Susanah Margaret, daughter of the Rev. C. T. Arnold, a Master at Rugby. They lived on in Cambridge, and for some years Newall worked at the Cavendish Laboratory, where, in 1884, his friend J. J. Thomson began his distinguished tenure of the Cavendish Professorship. From 1886 to 1890 Newall held the post of demonstrator, being specially concerned with the more advanced teaching of Physics for Part II of the Natural Sciences Tripos.

In 1897 he published a paper on *The Phosphorescence of Rarefied Gases*, in which he applied his results to the problem of nebulae. In 1901 he went to Sumatra and in 1905 to Algeria to observe solar eclipses.

Meanwhile, in 1889, his father had presented his great telescope, with the dome and equipment, to the University of Cambridge. It was erected on a site adjoining the existing Observatory, and H. F. Newall was put in charge. In 1909 a Professorship of Astrophysics was created, with Newall as Honorary Professor. It is worthy of note also that when, in the same year, he was elected to a Fellowship of Trinity, he resigned the pecuniary emoluments and became a Fellow without dividend.

In 1911 his work and responsibilities were again increased. The Solar Physics Observatory was moved from South Kensington to Cambridge, and its control passed from the Board of Education to the University, which gave Professor Newall the direction of the work to be done.

For many years the chief research carried on was the spectroscopic observation of stars moving one way or the other in the line of sight. By the shift of their spectral lines the velocities of movement of the stars could be estimated, and by tracing reversals in the direction of the shift the double nature of binary pairs of stars could be detected and the periods of their revolution determined. Many useful measurements were thus made on these and allied subjects, some ten or twelve papers on the spectra of sun, stars and comets being published between 1900 and 1920, most of them by Newall alone, but some with the help of colleagues or pupils.

But perhaps the most striking result obtained with the 25-inch equatorial and a four-prism spectroscope was the resolution of the star Capella into two, a discovery described by Newall in 1899 and 1900, and made independently, but almost simultaneously, by Campbell at the Lick Observatory in California. The spectrum of Capella was seen to be composite, one component resembling the spectrum of the Sun and one being more like that of Procyon. By plotting the velocity of the solar component against time, Newall got a sine curve, showing a period of 104 days. The velocity reached 27 kilometres a second, and the relative orbit was at least 52 million miles. The two components of the pair were found to be nearly equal in mass and appeared not very different in brightness.

Newall was President of the Royal Astronomical Society from 1907 to 1909, and in 1910 he published a successful book on *The Spectroscope and its Work*. In 1928 he resigned his Chair and became Emeritus Professor.

For the convenience of his work he built a pleasant house on a beautiful site at Madingley Rise, near the Observatories. There he and Mrs. Newall dispensed much hospitality, especially to the musical.

Both Newall and his wife were fond of horses. Newall kept a pair, and then a single horse, long after everyone else had given up horses and carriages for cars. He also owned, and for some time farmed, a small holding near his house.

The first Mrs. Newall died in 1930, and in 1931 Newall married Dame Bertha Surtees Phillpotts, the eminent Icelandic scholar, who also died in the following year.

Newall was a handsome man with great charm of manner. His friends were devoted to him, and they included not only the few approaching his own age who still survive, but many younger people also.

W. C. D. DAMPIER.

ANTHONY CHARLES SHEARMAN

DR. SHEARMAN was fatally injured in an accident at a Home Guard demonstration on 9 January 1944. His death, at the early age of 23 years, terminated a career which, although tragically short, had already given ample evidence of his ability to make a useful contribution to physics.

Shearman, a Londoner by birth, received his early education at Latymer Upper School, and from there obtained an exhibition to the Royal College of Science in 1938. In 1940 he qualified for the Associateship of the college in physics and started work in my laboratory on the physical properties of plastics. The following year he graduated as a B.Sc. in Honours Physics and also received the Diploma of the Imperial College for original work. In 1942 he was awarded the Ph.D. (London) degree for a thesis on the relation between the physical properties of plastics and their molecular structure. His published contributions are a paper to the *Proceedings of the Physical Society* on the photo-elastic behaviour of plastics and an article on the physics of plastics in the *Scientific Journal of the Royal College of Science*.

During the last two years of his life his research work was associated directly with the war effort and had achieved results of definite value. In all his work he combined a steadily maturing theoretical knowledge with thoroughness and enthusiasm both in the laboratory and in the field. As Student and Fellow he had been a member of the Physical Society since 1938, and was also an Associate of the Institute of Physics.

Of a happy disposition, Shearman was generally liked, and he entered wholeheartedly into the student activities of the college, being elected President of the Royal College of Science Union in 1940. He was a good athlete and was at different times Captain of Association Football and Athletics in both the Royal College of Science and Imperial College Clubs. He was also an active member of the Home Guard since early

L.D.V. days, and was a sergeant-instructor at the Melbury Training School, where his experimental lectures on service explosives constituted a high-light in the Home Guard instructional cadre courses.

Perhaps the most outstanding traits in Shearman's character were an intellectual stability and a sound judgment which won for him a degree of respect usually reserved for older men. His vital personality will be sorely missed by his many friends.

Shearman was married in 1942. G. I. FINCH.

ARTHUR WILLIAM CLAYDEN

Arthur Willliam Clayden, the first Principal of University College, Exeter, born at Boston in Lincolnshire on 12 December 1855, was the son of P. W. Clayden, sometime editor of one of the more famous London daily papers. He was educated at University College School and at Christ's College, Cambridge. After a period as science master at the old Bath College he was appointed University Extension Lecturer in 1887, and this was followed by his appointment as principal at Exeter in 1884. He retired in 1920 and, after spending some time as lecturer in meteorology at Cambridge, he removed to Parkstone, in Dorset, where he died on 21 February 1944. To Clayden fell the formidable task of starting and guiding the college at Exeter from its initial, modest collection of evening classes, but when he retired the foundations of the present institution were sound. His work was difficult and required considerable tact.

Although he possessed considerable administrative ability, he was most happy when engaged in original work. Keenly interested in astronomy, meteorology, geology and mineralogy—as well as physics—he was skilled in the construction of apparatus for his various researches. His publications on these subjects are numerous, and among them his book on *Cloud Studies* is the most important.

In private life he was a skilled artist and a man of wide humanity. Fundamentally a humble gentleman, he was at his best in the society of intimate friends, whom he would entertain with interesting conversations on a diversity of subjects.

He leaves a widow, to whom he was devoted, a son and a daughter. F. H. N.

REVIEWS OF BOOKS

Elastic and Creep Properties of Filamentous Materials and other High Polymers, by Herbert Leaderman. Pp. xii+278. (Washington, D.C.: The Textile Foundation.)

The classical researches of Weber and Kohlrausch on the elasticity of silk, glass and metal filaments provided the data for Boltzmann's and Maxwell's theories of the elastic after-effect. Boltzmann, in his Superposition Principle (which determines the deformation at any instant as an integrated effect of the previous loading history), embodied the elastic properties in a mathematical equation, whilst Maxwell, using springs and dashpots, catered for those who desired a mechanical model. With the development of modern research on fibres, attention has again become focussed on the subject of imperfect (non-Hookean) elasticity, for a consistent structural theory for fibres must be adequate to explain their observed elastic behaviour.

Dr. Leaderman has done a good deal of experimental work in a very restricted field: the time effect associated with the extension of fibres under small constant loads and their recovery after removal of the load. This book is chiefly a record of some of his experiments of this kind carried out on silk, viscose and acetate rayons, and nylon, and an attempt to interpret his results both classically and in terms of modern structure theory. In most of his work the extensions realized are confined to some 1 % at most ; that is, he is working in what is usually called the " Hooke's law region ". This reduces considerably the importance of his results, for it is not unreasonable to argue that all materials which show an elastic after-effect will behave in much the same way for small enough deformations ; and we find, in fact, that Dr. Leaderman lays a good deal of emphasis on the similarities between his results for fibres and those for glass and metals. In the one instance in which he overcomes his reluctance to treat a fibre less gently—a few of his nylon fibres were stretched by amounts up to about 8 %—he finds a different " pattern of creep behaviour ", rather, one gathers, to his surprise. This is taken to distinguish nylon from the other fibres, an unconvincing conclusion in the absence of data as to the behaviour of the others at higher extensions.

About a third of the text is devoted to an account of Boltzmann's theory and the mechanical models ; structural matters are scantily dealt with by comparison, having only 20 pages. Since he is relatively unconcerned with the differences between fibres, what Dr. Leaderman has to say is chiefly about the " fringe theory ", for his argument is that " creep " is associated with the secondary molecular forces between the chains in the non-crystalline regions of the fibre. Those interested in structure theory will probably find this part of the book the least satisfactory.

The remaining space is given over to the author's own painstaking and often ingenious experiments. Those on silk and the rayons were done at 65 % R.H. and 70° F., and in order to eliminate the setting effects which fibres under these conditions normally show, resort is made to a " mechanical conditioning " pre-treatment in which the fibres are first stretched under a constant load during 24 hours and then allowed to recover without load for an equal time ; subsequent extensions under smaller loads are then free from setting effects. Unfortunately, it appears (p. 132) that the " instantaneous Young's modulus " is a function of the conditioning load ; this leads to a rather disturbing suggestion that the pre-treatment has effects which are not so simple as would otherwise appear. The influence of temperature under dry conditions was also investigated for the acetate fibres, and a method of deducing a " heat of activation " for creep is described. Nylon receives the largest share of attention, and curiously enough it is only for this material that humidity effects are investigated, and this for a somewhat naïve reason—" the effect (of humidity) is relatively slight, and hence nylon is suited for an investigation over a wide range of R.H.".

Here and there throughout the book there occur statements which are of very dubious validity. Two examples will suffice : in one of the few references to wool the suggestion is made (p. 237) that its main chains are " closely though randomly coiled " ; and in a discussion of *high* elasticity (p. 96) one of the two possible mechanisms is stated to be the " elastic extension and bending of the primary valence bonds ". H. J. WOODS.

The Practice of Orthoptics, by G. H. GILES. Pp. 366. (London: Hammond, Hammond and Co., Ltd., 1943.) 25*s*.

Orthoptics is not a branch of vision with which physicists will normally be familiar unless they have themselves had to undergo orthoptic treatment. In the foreword to Mr. Giles's book, Sir David Munro writes : " Interpreted as the science of making straight the eyes . . . . . the term hardly conveys all that is intended. Since it has for its object the restoration of normal binocular vision, the science or art of orthoptics includes the restoration or education of stereoscopic vision, that high quality which enables one, using both eyes, to see objects in right perspective, to judge their distance, and, if moving, the speed at which they move ".

When we look at any object, the act of directing the visual axes of the two eyes to the same point of the object is so automatic that we are generally quite unaware that a remarkable degree of co-ordination between mind and muscle is required. If for any reason this co-ordination is disturbed, either because the mechanical forces acting on the eyes are not equally balanced or because of some mental aberration, then marked visual discomfort and eye-strain may develop, accompanied by errors in the stereoscopic sense, and in extreme cases by the appearance of a squint. Orthoptics is concerned with the treatment of patients with these symptoms, and in recent years the subject has become of very great importance. This importance has been engendered in part by the success of the methods which have been evolved and the consequent improvement now possible in the visual health of many members of the community, and in part by its employment in the training of pilots for the Air Force. If there is a tendency for the visual axes to diverge, accidents may be caused through the pilot flattening out his aircraft too soon when making a landing, since he judges the ground to be nearer than it actually is. On the other hand, if the axes are inclined to converge, the pilot is liable to fly into the ground. Training to secure a true balance between the eye muscles is thus literally a matter of life and death.

Mr. Giles's book is especially welcome because it embodies so much of his own experience, gained in the clinic at the London Refraction Hospital. While the diagnosis and treatment can, to some extent, be systematized, each patient requires individual consideration, and the many case histories reported in the book are, therefore, of special value. It is gratifying also that the book provides a further opportunity for giving publicity to the excellent work being carried out at the London Refraction Hospital.

Detailed accounts are given of the methods of testing and training and the means by which favourable cases for treatment can be selected. In so far as the book may be said to have a general theme, this may be described as the importance of the psychological approach to the problem and the large part which mental effort must play in the treatment. Indeed, one of the major aspects of the orthoptist's work is the need to inspire his patient with the desire and determination to persevere with the training. The author gives many examples by which interest may be maintained, one of which consists in playing a game of snap in which the patient views his own cards in one eye and those of his opponent in the other; this encourages the development of a high degree of simultaneous vision for form.

Mr. Giles' book is essentially a book for the specialist, although certain sections are of more general interest. There is a short chapter at the end in which the author gives an interesting and balanced discussion of the Bates method of treating eye defects, a method which was recently championed by Aldous Huxley. It is possible that some rearrangement of the chapters and sections might have avoided a good deal of repetition, in which the same instrument is referred to several times in a slightly different context, but that is a matter perhaps of individual judgment. The text is not always as clear as might be wished, and words are used rather loosely at times. We may note as an instance the sentence on page 189 : " Probably many sensations are psychic reactions ". If we overlook the fact that " psychic " generally has a spiritualist connotation and imagine " psychological " or " mental " put in its place, the sentence is still not correct, because *all* sensations are experienced through reactions in the brain. The following sentence or two reveal what was intended, namely, that the impression created by a visual sensation may be affected by the state of mind of the observer; but it is a pity not to make the point with greater clarity. But perhaps in these times such criticisms are luxuries in which we ought not to indulge. W. D. WRIGHT.

Introductory Magnetism and Electricity, by T. M. YARWOOD. Pp. vi+159. (London : Macmillan and Co., Ltd., 1944.) 2*s*. 6*d*. net

" Introductory " is the keyword to this small book, and would that more young people whose future is in the practical world of application, and not in the academic world of the research laboratory, might be taught along such lines. Empirical ? Yes. Vocational ? Yes. But with a good accompanying practical book (the author should produce one) the students would enjoy their study, and that would be good. As stated by the author, when once they have mastered basic principles, students can rapidly increase their knowledge of the subject both by theory and practice. The book is intended as a pre-Service training for cadets of the Air Training Corps who ultimately hope to join the Royal Air Force as wireless operators and mechanics, instrument repairers or electricians.

The order of presentation, which, on the whole, follows normal lines, is excellent. The magnetic field is not introduced until the third chapter (time is rightly saved by omission of the tangent galvanometer and magnetometers), while the electric field is discussed in the tenth chapter along with capacitance and condensers. The last chapters deal respectively with telegraph and telephone, valves and rectifiers and the basis of radio communication.

All this for half-a-crown, and in war time—which perhaps explains why the cover is limp and the numerous figures illustrating the text unnumbered. M. D. W.

Vision (wall chart 40 × 30 inches) ; *Protective Mechanism of the Eye and Sight as Function of the Brain* (wall chart 40 × 30 inches). (New York : Rudolf Schäck; London: Adam, Rouilly and Co.) 25*s*. each.

The chart on *Vision* shows axial sections of emmetropic, myopic and hyperopic eyes in their orbits. A parallel pencil of light entering the emmetropic eye is shown focusing upon the retina. In the diagram of the myopic eye a parallel pencil in black focuses before the retina, and one in red, made divergent by a negative lens, focuses at the retina. The hyperopic eye is shown with a pencil of light diverging from a near point and focusing behind the retina, while a similar pencil in red, after passing a positive lens, focuses at the retina. The use of light from a near point in the hyperopic case only may be confusing to the student, and there appears to be no reason for treating this case differently from the others. These three diagrams may be helpful in showing the fundamental structure and function of the eye to students of elementary physics, but the general value of the charts seems doubtful.

The other chart, showing an anatomical drawing of the orbits, protective mechanism and brain, although elaborate, is not sufficiently complete or accurate for the student of ophthalmology who has to study the anatomy of these parts. For instance, the orbital muscles and optic nerve are shown too thick in every case. The chart of *Sight as Function of the Brain* gives little useful information beyond showing that the nerve fibres from the nasal sides of the retinae cross at the chiasma. The representation of these crossed fibres terminating in the thalamus, while the uncrossed fibres pass direct to the cerebral cortex, is incorrect.

The charts are mounted on linen, the colouring is clear and the general production is good. E. F. F.

The Mechanism of the Electric Spark, by Leonard L. Loeb and John M. Meek. Pp. xi + 188. (Stanford University Press, California; London: Humphrey Milford, Oxford University Press.) $3.50.

In this monograph the authors give an account of the phenomena associated with the spark discharge ; both experimental and theoretical aspects are dealt with.

The opening chapter is concerned with experiments testing Townsend's formula; the region where the Townsend theory breaks down is carefully considered. In this region (where the product of pressure and spark length exceeds a certain value) the time of the discharge is far too short for the positive-ion mechanism of the Townsend theory to play any part ; this is replaced by the streamer mechanism (Chapter II) in which photons and photo-electrons play the predominant rôle. The experimental basis of the theory is carefully set out and the theory is then applied to detailed phenomena observed in the spark discharge. The final chapter deals with the calculation of breakdown potentials for gaps of various geometrical shapes ; the calculation is based on a quantitative (though rather empirical) formulation of the theory due to Meek, and the agreement with experiment is impressive.

This account—the first detailed consideration of the streamer mechanism—will be stimulating to research workers concerned with gas discharges and instructive to non-specialists. It can be recommended to all physicists. M. B.

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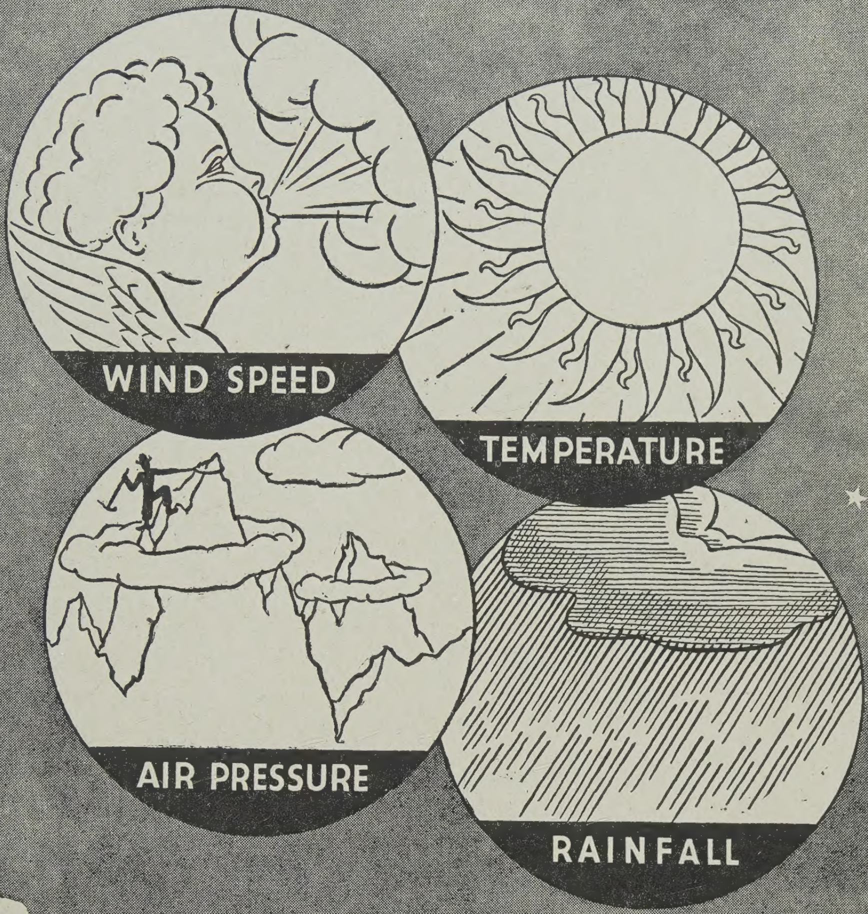

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